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THE

PHYSICAL REVIEW.

IONIZATION AND EXCITATION OF RADIATION BY ELECTRON IMPACT IN MERCURY VAPOR AND HYDROGEN.

By Bergen Davis and F. S. Goucher.

Mercury Vapor.

Introduction.—It has recently been pointed out by Van der Bijl[1] that the regular Lenard method for the direct determination of the ionizing potentials of different gases and vapors, in particular mercury vapor, is open to an objection which has not been considered by the experimenters hitherto employing this method. The objection is based on the fact that the positive charging up of the collecting electrode may as well be due to a photo-electric emission of electrons from it, under the action of the ultra-violet light emitted by the impacted atoms of the gas or vapor, as to the formation of positive ions by impact. This fact could not be determined from the curve shape since the number of radiating sources (intensity of radiation) and the positive ions produced would both be proportional to the number of impacts.

The possibility that this is the case in mercury vapor at a voltage less than the true ionizing voltage is rendered highly probable, because of the nature of the experimental results obtained by Tate,[2] Goucher,[3] and McLennan and Henderson.[4] Tate and Goucher have shown that below the region of 10 volts an effect is obtained setting in at 4.9 volts, but that this is small compared to the effect occuring at 10+ volts.

It had previously been shown by Franck and Hertz[5] that impacts in mercury vapor were elastic up to a certain minimum energy of the im-

[1] Phys. Rev., pp. 173–175, Feb., 1917.
[2] Phys. Rev., pp. 686–687, June, 1916.
[3] Phys. Rev., pp. 561–573, Nov., 1916.
[4] Proc. Roy. Soc., A, Vol. 91, 1915.
[5] Verh. d. D. Phys. Ges., Vol. 11, p. 512.

pacting electrons, viz., 4.9 volts, and that at this voltage the electrons lost their energy and at the same time emitted the radiation of wave-length $\lambda = 2536.7$ Å., the frequency of which was connected with the voltage (4.9) by the quantum relation $Ve = h\nu$. They had assumed that this loss of energy was accompanied by ionization. McLennan and Henderson extended this work and found that in mercury vapor this single line $\lambda = 2536.7$ Å. alone apparently was emitted up to a value of the voltage slightly greater than 10 volts, but that the many lined spectrum of mercury suddenly appeared if the voltage was increased much beyond this value. They also pointed out that this value 10+ volts is near that calculated from the quantum relation, $Ve = h\nu$, when the frequency taken is that of the head or shortest wave-length of the Paschen combination series of the mercury spectrum $\nu = 1.5S - mP$, viz., 10.4 volts; whereas the line $\lambda = 2536.7$ Å. is the first or longest wave-length of the second subordinate group of this same series, viz., $\nu = 2p - mS$. From theoretical considerations then, in light of the Bohr theory, McLennan was led to question whether ionization really took place at 4.9 volts, or only at 10+ volts at which the many lined spectrum was emitted. He was led to conclude however by his own (McLennan and Keys)[1] experiments on the conductivity of flames in which mercury vapor was present in a state of emitting only the line $\lambda = 2536.7$ Å., that ionization really did take place at this voltage and that therefore there seemed to be two types of ionization in mercury vapor. It should be noted however that the flame conduction experiments are open to the same criticism as those employing the direct method of Lenard.

It may be pointed out that there are no theoretical grounds for believing that there should be two types of ionization in mercury vapor; nor yet why, if a single line was emitted without ionization at its corresponding voltage, the other lines were not emitted at their corresponding voltages, instead of appearing altogether when ionization had taken place as the experiments of McLennan seemed to indicate. McLennan looked carefully for the other intense line in the series, viz., $\lambda = 1849$ Å., which is the longest wave-length of the principal series, $\nu = 1.5\ S - mP$, but was unable to find any trace of it.

All these facts rendered it highly desirable to determine whether or not the effects occuring below 10.4 volts were due to ionization or to the emission of ultra-violet light from the bombarded atoms, and whether or not positive ionization actually took place at 10.4 volts. For the purpose of testing with regard to these possibilities, the following modification of the Lenard method was proposed by one of us (Goucher).

[1] Proc. Roy. Soc., A, Vol. 92, p. 591, 1916.

Apparatus.—The modification consisted essentially in the introduction of a second gauze, *C*, Fig. 1 in the apparatus employed in the regular Lenard method and described in detail by Goucher; where *A* is the platinum equipotential surface electron source; *B* the platinum gauze through which the electrons from *A* are accelerated; *D* the collecting electrode of aluminum.

The gauze *C* was of rather large copper wire and coarse mesh, and was supported by the tight-fitting flange of brass in the glass part as shown. The arrangements were otherwise quite the same as those employed in the vessel used by Goucher, with the exception of the palladium tube *P* sealed in for the purpose of admitting hydrogen into the apparatus when desired.

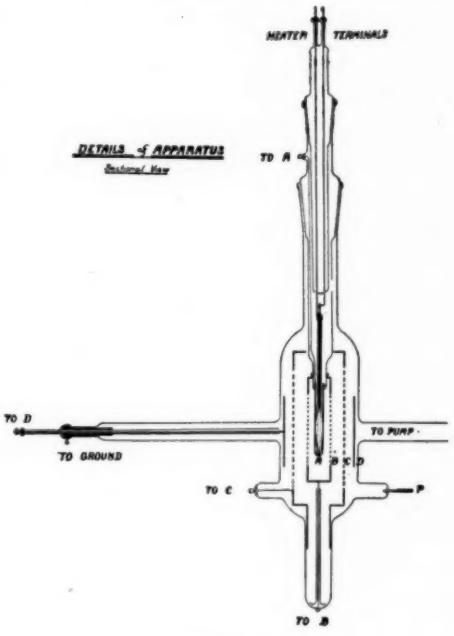

Fig. 1.

All joints not of glass were ground and sealed with De Khotinsky cement, the heater leads being also sealed in with this cement.

The vessel was connected through a large $\frac{3}{4}$ in. exhaust tube, a liquid air trap, and a large stop-cock, furnished with a capillary by-path, to a mercury diffusion pump of the Langmuir type, and to a McLeod gauge.

The electrical measurements were made by means of a suitably shielded electrometer connected to *D* and sensitive to about 500 div. per volt. The potentials were applied and maintained by means of dry cells and suitable potentiometer connections, and were measured by a Siemens and Halske standard voltmeter.

Method.—The procedure in making measurements was essentially that employed in accordance with the Lenard method.

A field V_1 was impressed between *A* and *B*, Fig. 1, in such direction as to accelerate the electrons from *A* through the gauze *B*; a field V_2 was maintained between *B* and *C* in such direction as to oppose the passage of these electrons in the region *BC* and just enough larger than V_1 to prevent the electrons from reaching *C*. The departure from the Lenard method consisted in the maintainance of a third and constant field V_3

between C and D throughout the measurements, but just as in the Lenard method the rate of charging up of D was measured for different values of the voltage V_1, $V_2 - V_1$ being maintained constant. The shape of the current curve thus obtained and its intercept with the voltage axis was, as in the case of the Lenard method, used as a basis for the interpretation of the results.

The function of V_3 was to control the field between C and D, it being possible to maintain it either in the same direction as V_2 or in the opposite direction, thereby furnishing a means of distinguishing between a photo-electric charging up of D, and a charging up due to the production of positive ions in the region BC. For if V_3 be made smaller than V_2, positive ions formed in the region BC will be able to reach D and consequently will have a tendency to charge it positively whether V_3 be either in the same or opposite direction to V_2. Whereas, if the atoms of the mercury vapor are stimulated to emit radiation, both C and D will be in the path of such radiation, and would consequently be capable of emitting photo-electric electrons, so that D would charge up due to this cause, and the direction of this charging up of D would be determined by the direction of the field V_3. If V_3 were in the same direction as V_2 electrons would be extracted from D and driven to C (or through it into the region BC beyond), while if V_3 were in the opposite direction to V_2, the emission of electrons from D would be prevented, and part of the electrons emitted from C would be carried to D, causing it to charge up negatively. The relative rates of charging up of D for these two directions of V_3, for any given voltage V_1, would of course depend on the relative strength of electron emission of C and D under these conditions. It is evident that they would follow the same law of increase with increasing values of V_1, since the intensities of the radiation falling on C and D should always be in the same ratio.

It is evident that if C and D are connected together we would have the equivalent of the regular Lenard method, and we see why in this case we would have no means of distinguishing, from the shape of the current curves, as to whether it is caused by radiation from the impacted atoms or to actual ionization of the gas. For, if the charging up of D were due to radiation, the intensity of electron emission from CD would be proportional to the number of atoms stimulated to emit radiation by impact, whereas if it were due to positive ions from region BC, the number of such ions would be proportional to the number of impacts resulting in ionization.

The procedure then in the application of this method for the purpose of distinguishing between these two causes, consists in maintaining a

field V_3 in a desired direction between C and D. The field V_3 is small compared to V_2. The field V_1 and V_2 are applied in their proper directions, the difference $V_2 - V_1$ being kept constant, and the rate of charging up of D for different values of V_1 is measured. The current voltage curves, for V_3 in the same or opposite direction to V_2, may be thus obtained and compared. Should the curves show a negative charging of D when V_3 is oppositely directed to V_2, we may conclude that at least the effect of radiation is greater than that of ionization, and if the curve continues to increase in the negative direction for increase of voltage V_1, we must attribute this increase to impacts resulting in radiation, for the tendency of ionization would be to cause an increase of current in the positive direction.

The method can be further extended to the study of radiation alone, by making V_3 greater than V_2 and in the opposite direction to it, thus preventing the positive ions that may be formed in the region BC from reaching the collecting electrode D. The charging up of D in this case will be due to the electrons emitted from C by the ultra-violet radiations and carried to D by the field V_3. The shape of the negative current curve with different values of V_1 will then serve as a basis for an interpretation of the nature of the radiation emitted by the atoms of mercury vapor when impacted at various voltages.

Results.—For the purpose of making measurements in mercury vapor liquid mercury was introduced into the measuring vessel and contained in the part marked "To B," Fig. 1. The heat from the electron source A was sufficient to produce the desired pressure of mercury vapor for most measurements, but the vessel was enclosed in a heat insulating box when higher pressures were desired. The pressures usually employed were probably less than .01 mm., estimating from the temperature of the vessel at the time of making the observations.

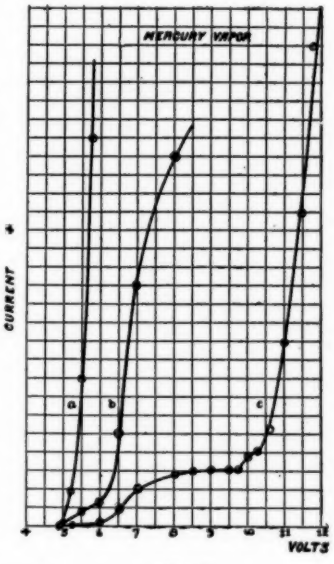

Fig. 2.

The diffusion pump was kept running continuously to carry off any traces of other gases than mercury vapor. The quantity of permanent gas present was always too small to give a reading on the McLeod gauge.

Fig. 2 shows the current curves obtained in accordance with the regular

Lenard method (C and D connected together), where (a), (b) and (c) were obtained with decreasing electron emission from A, and over increasingly wider range of voltages. Curve (a) shows the sharp break at 4.9 volts, and is the same kind of curve as that previously obtained by Goucher. Curve (b) shows a marked increase of the current between 6 and 7 volts, while curve (c) shows this same increase and in addition a discontinuity at 9.8 volts and a very sharp rise in current intensity at 10.3 volts. This value 10.3 volts is very close to 10.4 volts as calculated from the head of the Paschen series. The discontinuity at 9.8 volts which occurs at twice the value 4.9, is what should be expected in consideration of the elastic nature of the impacts of electrons having an energy less than that due to 4.9 volts; and this would be true whether the energy lost at 4.9 volts were transferred into radiation or produced ionization. This energy loss would occur again at twice this voltage, viz., 9.8 volts, producing an increase either in the intensity of the radiation or ionization at values beyond this.

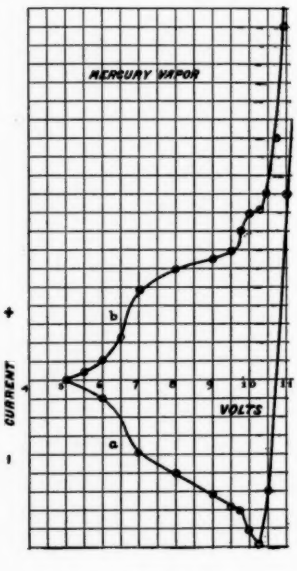

Fig. 3.

The curves obtained, when the charging up of D alone was measured, with a field V_3 of 1.5 volts maintained between C and D, are shown in Fig. 3. Curve (b) was obtained with V_3 in the same direction as V_2, and curve (a) with V_3 in the opposite direction to V_2. Since curve (a) shows a negative charging of D, increasing with increase of applied voltage V_1 up to a voltage of 10.3+, where there is a sharp positive increase, we can fairly attribute the effects below this point to a photo-electric emission of electrons from C. The production of positive ions in region BC would cause an increasing tendency to make D charge positively with increasing values of V_1. Since curve (b), up to 10.3+ volts, shows a positive charging of D in accordance with practically the same law of increase as shown in (a), we can likewise attribute this part of the curve to photo-electric emission of electrons from D. We may conclude from these results that the corresponding portions of the curves obtained by the regular Lenard method (Fig. 2) were also due to photo-electric action on the collecting electrode caused by radiation from the impacted atoms of mercury vapor.

The strong positive charging of D in both cases, (b) and (a) Fig. 3,

above the value 10.3+ volts, we can attribute only to the production of positive ions in the region BC, and since this value, within the limits of experimental error, is equal to the value calculated from the frequency of the shortest wave-length of the spectral series, viz., 10.4 volts, it is fair to conclude that this latter is the true ionizing potential of mercury vapor.

Since the parts (a) and (b) of the curves (Fig. 3) are due to radiation, the question arises as to the cause of the rise of these curves between 6 and 7 volts. Attention has been called to the fact that the other strong line in the Paschen series is the wave-length $\lambda = 1849$ Å. This line was sought for by McLennan but not found. The value of the voltage corresponding to this line as calculated from the quantum relation is 6.7 volts. It seems probable that the increase in the intensity of the radiation between 6 and 7 volts is due to this cause.

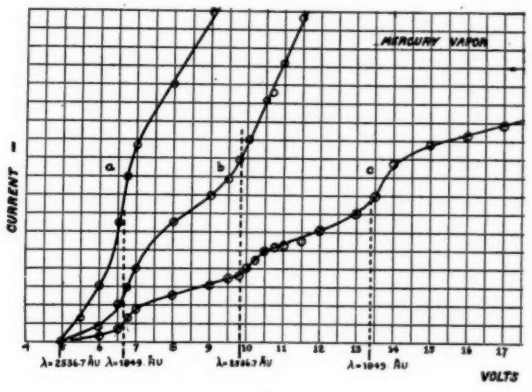

Fig. 4.

Since the curves obtained show that the radiation occuring at 4.9 volts will produce a sharply defined discontinuity at twice this value (9.8 volts), we would expect that if additional radiation were emitted when electrons lose their energy at 6.7 volts, such electrons would be capable of losing their energy a second time at twice this voltage, viz., 13.4 volts, and consequently there should be a second rise in the radiation curves beginning at this voltage.

For the purpose of testing this point V_3 was made large (about 20 volts) and in the opposite direction to V_2, and a curve showing the negative charging of D with increasing values of V_1 over a range greater than 13.4 volts was obtained. The curves obtained with this arrangement of voltages are shown in Fig. 4, where (a), (b) and (c) are for decreasing electron emission from electron source A. The dotted lines show the points

at which rises in the curves should take place on the assumption that the two lines $\lambda = 2536.7$ Å. and $\lambda = 1849$ Å. are produced at their respective voltages. The shape of the curve (*c*) certainly indicates the existance of such effects.

The fact that there appears to be no marked increase in radiation at the ionizing voltage (10.4) is quite significant. It indicates that the energy of the impacting electron had gone into separating the electron from the sphere of action of the atom, and in so doing had produced no radiation. This suggests that the strong increase in radiation coincident with the production of the many lined spectrum observed by McLennan and by Richardson is due to recombination and not to ionization. It should be noted that the pressure of mercury vapor in these experiments was small, and that the chances for recombination are therefore small as compared to the conditions employed by those experimenters.

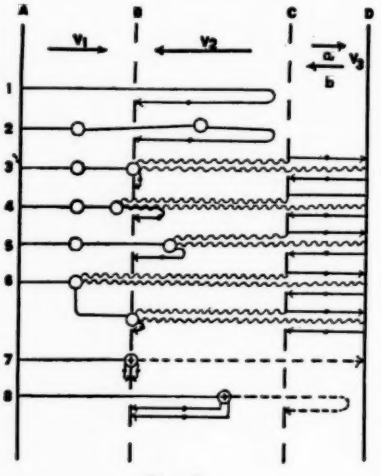

Fig. 5.

The foregoing interpretation of the results obtained for mercury vapor is more easily understood by a consideration of the schematic diagram, Fig. 5, where *A* represents the equipotential source of electrons and *B* the gauze through which these electrons are accelerated by the field V_1. The arrows represent the directions in which electrons would move in the various fields. The extra gauze is represented by *C*, and *D* is the collecting electrode. The fields V_2 and V_3 are maintained between *BC* and *CD* respectively. The difference $V_2 - V_1$ is kept constant and just large enough to prevent electrons from *A* reaching *C*. The field V_3 is also constant and arranged to carry electrons from *C* and *D* or vice versa as represented by the arrows.

Consider the possible history of electrons with increase of voltage V_1. At all voltages an electron may at this low pressure take a path as represented by (1) in which it makes no collisions with the atoms. If it does however make such collision and the energy is less than a given minimum corresponding to a voltage V_0 (4.9), the impacts are elastic as shown by Franck and Hertz, and the path of an electron making such impacts would be represented by (2), where the circles represent impacted atoms. When V_1 becomes equal to the minimum voltage V_0 at which

the electron will lose its energy, and if it is assumed that this energy will appear as radiation, some of this radiation will fall on both C and D causing photo-electric emission of electrons. These latter electrons will move in the field V_3 according to its direction (a or b). This situation is represented by (3) in the figure.

As V_1 is increased beyond V_0 an electron is capable of producing radiating atoms in an increasingly wider range on either side of the gauze B, thus proportionately increasing the intensity of the radiation reaching C and D. This situation is represented by (4) and (5). When V_1 becomes equal to $2V_0$, impacts half way between A and B will cause the electron to lose its energy, but it will be capable of again acquiring enough energy to cause another atom to radiate in the region of the gauze B, as represented by (6); so that beyond $2V_0$ some of the electrons would have this double capacity for causing atoms to radiate and therefore we should expect a corresponding increase in the intensity of radiation at a value of V_1 equal to $2V_0$.

If ionization takes place at or beyond B in the region BC, the positive ions so formed would be carried to D irrespective of the direction of V_3, so long as this latter is smaller than the fraction of V_2 run through by the positive ion before reaching C. Therefore at this point we should expect a tendency for D to charge positively irrespective of the direction of V_3. This situation is represented by (7). The transport of positive ions to D can be prevented however by making V_3 larger than V_2 so that no positive ions can reach D from the regions BC as shown in (8). The effects due to radiation alone can thus be studied even at large values of V_1.

It may be objected that since V_2 is slightly greater than V_1, electrons photo-electrically emitted from C or D would be capable of producing positive ions in the region BC before those from A could do so. This is of course true, but the number so doing is so small that it does not mask the effect under these experimental conditions. This was shown experimentally by increasing the difference $V_2 - V_1$, and also by increasing the pressure of the mercury vapor. There was an appreciable tendency to charge positively below 10.3 volts. The point at which the curve started to rise depended on $(V_2 - V_1)$, but in no case did it mask either the discontinuity found at 9.8 or 10.3+ volts, which are of course independent of $(V_2 - V_1)$. It may also be objected that since V_3 is large compared with V_1 and V_2, that it would be capable of producing ions and additional radiation in the region CD. But since these ions and radiation could only be produced by the electrons emitted from C by the action of the radiation from the impacted atoms in AB and BC, such ionization and

radiation would tend to increase the magnitude of the breaks in the curves, which occur at particular values of V_1.

The results of these experiments may be summarized as follows:

(*a*) Radiation is emitted without ionization at an impact voltage of 4.9 volts. This voltage corresponds to the frequency of the first line $\lambda = 2536.7$ Å. of the Paschen combination $\nu = 2p - mS$, as has previously been pointed out.

(*b*) An increase in the intensity of the radiation takes place at an impact voltage of about 6.7 volts. This voltage corresponds to the frequency of the first line ($\lambda = 1849$ Å.) of the principal series $\nu = 1.5S - mP$ of this combination.

(*c*) Ionization by impact, without an apparent increase in radiation, occurs at an impact voltage of about 10.4 volts. This voltage corresponds to the head or shortest wave-length of this same principal series.

These results are of considerable interest when considered from the point of view of the Bohr theory of the atom. The definiteness of the results are due to the fact that the impacts in mercury vapor are perhaps completely elastic. That is, an electron loses no energy at impact with a mercury atom, unless either radiation or ionization is produced, in which case the entire energy of the electron goes into the radiation or the ionization, and none is absorbed by the atom.

When the atom is impacted by an electron running through 4.9 volts, its energy is transferred to an electron of the atom, lifting it we may suppose from its equilibrium position to some ring farther from the nucleus, and storing this energy in the potential form. Upon the return of this electron to its equilibrium position this energy appears as radiation ($\lambda = 2536.7$ Å.) in accordance to the relation $Ve = h\nu$.

When the atom is impacted by an electron having an energy corresponding to 6.7 volts, an electron in the atom is lifted from its position of equilibrium to some other ring still farther from the nucleus, and its energy stored in the potential form. Upon the return of this electron, its energy appears as radiation ($\lambda = 1849$ Å.) in accordance with the above energy relation.

One considerable difficulty with this view of the process of emission of radiation is that the other lines of this spectral series should appear at their corresponding voltages. They apparently are not produced in sufficient intensity to affect the curves obtained in these experiments. The intensities of these other lines are weak compared to the intensities of the two strong lines just referred to, when the radiation is observed from the usual electrical discharge in mercury vapor. If the energy emitted at each frequency corresponded to its voltage ($Ve = h\nu$), then

all the lines should be intense, and their intensities should progressively increase toward the head or shortest wave-length of the series.

When the atom is impacted by an electron having energy corresponding to 10.4 volts, an electron in the atom is lifted entirely from the atom and removed from its sphere of influence. This electron is then free and the atom is ionized. No radiation is then produced, as the electron does not return to the atom. When the conditions are such that this (or some other) electron may return to the atom (recombination) then radiation is emitted. Experiments on the electrical discharge in mercury vapor indicate that under these conditions not only is the Paschen spectral series emitted, but the entire mercury spectrum including the visible.

Much of the phenomena of electrical discharge in gases indicate that the greater part of the emission of radiation takes place at recombination and not at ionization. We might mention for illustration the fact that the most intense light from the usual vacuum tube discharge is emitted from the cathode glow, where the electrical field is small, the concentration of ions greatest and the recombination of the ions is far in excess of their rate of production; while on the other hand in those parts of the discharge in which the ionization is in excess of the recombination the emission of light is small. Some recent direct experiments of Child[1] indicate also that a part at least of the emission of light from mercury vapor is due to recombination of the ions.

Hydrogen.

Introduction.—It seemed desirable to apply the method employed for mercury vapor to an investigation of hydrogen as well, on account of its theoretical interest in connection with the Bohr theory of the atom. The value of the ionizing potential for hydrogen has been found by Franck and Hertz[2] and also Pavlow,[3] using the regular Lenard method, to be 11 volts. This is in agreement with some recent work of Bishop,[4] using the same method, who also has found by extending the current curve over a wider ange of voltage, that there is apparently a second type of ionization at 15.8 volts. Neither of these values are in accord with the theoretical voltages, calculated from the Bohr Theory. The theoretical value yielded by this theory would be that corresponding to the head or shortest wave-length of the series given by

$$\nu = N\left(\frac{1}{T_2^2} - \frac{1}{T_1^2}\right),$$

where $T_2 = 1$. $T_1 = 1, 2, 3$ which is the series observed by Lyman.

[1] Phys. Rev., Jan., 1917.

[2] Franck and Hertz, Deutsch Phys. Ges., Vol. 15, 1913.

[3] Pavlow, Proc. Roy. Soc., Vol. 90, 1914.

[4] Bishop, not yet published.

Using the value of N,

$$N = \frac{2M^2me^4}{h^3} = 3.26 \times 10^{15}.$$

as given by the Bohr theory, we can calculate the different frequencies of this series; and from the $Ve = h\nu$ relation can calculate the value of voltage corresponding to the different members. This gives a value 10.2 volts as that corresponding to the first line or longest wave-length, and 13.6 volts as that corresponding to the shortest wave-length. This value then in the light of the Bohr theory should be the ionizing voltage. It therefore seemed desirable to redetermine the values for hydrogen by the application of this method to see whether or not the effects obtained at 11 volts were due to radiation and not to ionization; and whether either the radiation or ionization had any connection with the above values calculated from the Bohr theory.

The apparatus was the same as that used for the investigation of mercury vapor. A stream of hydrogen was continuously passed through the observation vessel by means of the palladium tube P. This was heated by a gas flame and the pump was kept running. The pressure of the hydrogen could be maintained as desired by regulating the flame that heated the palladium tube.

The vessel was kept free from mercury vapor by means of liquid air applied to the liquid air trap between the vessel and the pump.

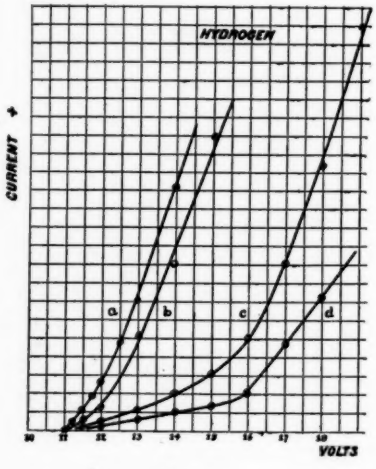

Fig. 6.

The complete elimination of mercury vapor could be tested by the disappearance of the radiation effects characteristic of mercury vapor below 10 volts which have just been described.

Results.—With the pressure of about .01 mm. and the potential V_3 small and arranged so as to draw electrons from C to D, the potentials V_1 and V_2 were arranged to give curves of same type (*a*, Fig. 3) as found in mercury vapor. With this arrangement of V_1, V_2 and V_3, if there were no ionization and only radiation, a negative current would have been observed. The curves actually obtained were all positive and are shown in Fig. 6, where *a*, *b*, *c* and *d* represent results with diminishing electron emission from equipotential source A. This indicates that

though there may have been radiation, the effects of this radiation were more than overcome by the positive ions formed by impact in region *CD*. These results confirm those of Franck and Hertz, who interpreted their experiments as showing ionization by impact at 11 volts. They also agree with the results of Bishop who found a break in the curve at about 15.8 volts, indicating a second type of ionization at this voltage. These curves (Fig. 6) might be due to ionization alone or to a combined effect of ionization and radiation, if the ionization effect were greater than the radiation effect.

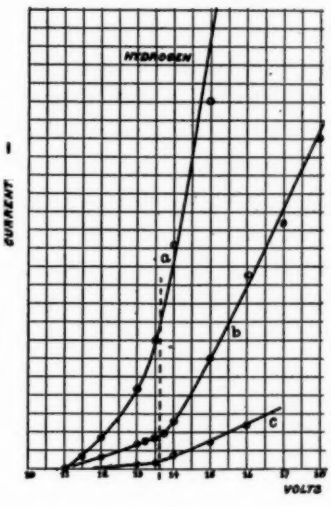

Fig. 7.

The existence of a radiation without disturbance due to ionization may be tested for by an arrangement of potentials similar to that by which the curves (Fig. 4) were obtained in mercury vapor. The potential V_3 was made larger than V_2 (it was made about 20 volts) and directed so as to stop and turn back the positive ions coming through *C* toward *D*. At the same time, the photo-electric electrons emitted by radiation falling on *C* would charge *D* negatively.

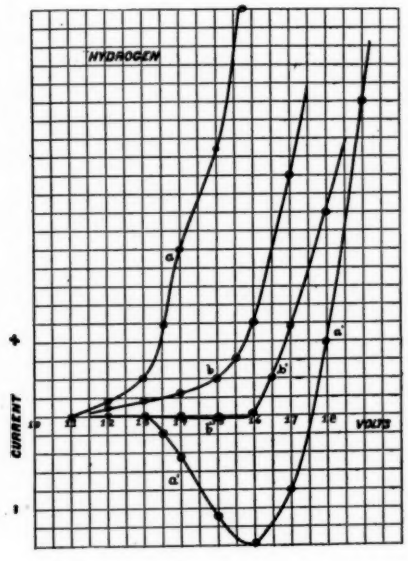

Fig. 8.

The curves thus obtained are shown in Fig. 7, where *a*, *b* and *c* are curves for diminishing electron emission from the electron source *A*. These reults reveal the striking fact that there are two types of radiation from hydrogen. The one type occurs at the ionization potential of 11 volts and the other at 13.6 volts.

The effects due to radiation may be increased and at the same time those due to ionization may be decreased by increasing the pressure of the hydrogen. The curves in Fig. 8 were obtained with a pressure of .3 mm. Curve *a* was obtained for V_3 equal to 1.5 volts, and in the same direction as V_2, while

a' was obtained with V_3 at 1.5 volts and in the opposite direction to V_2. The curve a shows the combined effects of ionization and radiation, while curve a' shows the difference between the ionization and the radiation effects.

The curves b, b' were similarly obtained at lower pressures, where the radiation effects were not so strong as at higher pressures. The ionization and radiation effects nearly neutralize (b') until a voltage of about 15.8, where the second type of ionization begins, when the ionization predominates.

At the pressure of .3 mm., the radiation and ionization effects just neutralize from 11 to about 13 volts when the radiation predominates to about 15.8 volts at which point the second type of ionization sets in, and then the ionization effects predominate.

These experiments show the following facts:

(a) Both ionization by impact and emission of radiation occur at 11 volts.

(b) A second type of ionization by impact without increase of radiation occurs at about 15.8 volts.

(c) A second type of radiation without an increase of ionization is emitted at 13.6 volts.

These facts show a greater complexity than the simple Bohr theory of the atom would predict, but are not inconsistent with it.

As has been indicated in a previous paragraph, by means of this theory together with quantum relation the voltage corresponding to any frequency may be readily calculated.

The voltage corresponding to the head or shortest wave-length of Lyman series ($T_2 = 1$ and $T_1 = \infty$) is 13.6 volts. The voltage calculated in the same way for the tail or longest wave-length of this same series ($T_1 = 2$) is 10.2 volts.

There is thus a marked difference in the behavior of hydrogen and mercury vapor. This latter gas showing radiation at a voltage corresponding to the longest wave-length and ionization without radiation at the head of the series. There is no radiation from hydrogen at 10.2 volts, which corresponds to the tail or longest wave-length of the series. This may be due to the fact that the radiation of this frequency is very weak or that some of the energy of the impacting electron is transformed into kinetic energy of the hydrogen atom. This is quite probable since the impacts in hydrogen are not elastic as in mercury vapor.

The occurrence of a new type of ionization by impact at 15.8 volts instead of 13.6 volts which might be expected can also be accounted for on the hypothesis that the hydrogen atom has a certain affinity for an

electron. As the electron is displaced from the inner ring by the impact, the radiation emitted on its return will correspond to the change in the potential energy caused by the impact. When the impacting energy is that due to 13.6 volts the electron is lifted to the outer ring or boundary of atom and on its return emits the radiation of highest frequency. But this electron when displaced to the outer ring will not be free as in case of the mercury atom. If the hydrogen atom has an affinity for an electron (non-elastic), it will require an additional energy to separate the electron entirely from the atom (ionization). This additional energy will be represented by the difference in voltage (15.8–13.6). This difference of 2.2 volts is thus a measure of affinity of a hydrogen atom for an electron. An important result is the production of ionization at 11 volts. This fact presents some difficulty in view of the Bohr theory, but it may be due in some way to the diatomicity of hydrogen. We may perhaps assume that at the 11 volts impact, the two atoms are separated one from the other, and that the electron is taken away from one atom and attaches itself to the other in this process, the one becoming a positive and the other a negative ion.

It is hoped that we may be able to examine other diatomic non-elastic gases, to determine if they behave in a similar manner.

Phœnix Physical Laboratory,
Columbia University,
April, 1917.

A REACTIVE MODIFICATION OF HYDROGEN PRODUCED BY ALPHA-RADIATION.

BY WILLIAM DUANE AND GERALD L. WENDT.

IT is well known that the rays from radio-active substances produce chemical reactions. They decompose water, whether the water is in the liquid, solid or gaseous phase; they transform oxygen into ozone; they split up hydrogen sulphide and ammonia into their elements; they form hydrochloric and hydrobromic acid and ammonia from their elements, etc.

The investigations described in the following pages were undertaken in order to find out whether the rays produce an appreciable chemical change in the purest hydrogen obtainable.

SOURCES OF RADIATION.

The most suitable source of radiation for the purpose appeared to be a small "alpha-ray bulb" consisting of a glass sphere .5 mm. in diameter, filled with radium emanation. If the walls of the sphere are thin enough a large fraction of the alpha-ray energy passes through them, producing an intense radiation in its immediate neighborhood. Such a source also has the advantage that the radioactive substance does not come into contact with the chemical reagents under investigation.

The bulbs used in our experiments were filled in the laboratories of the Harvard Cancer Commission by a method previously described.[1] They usually contained about 35 millicuries of emanation.

PURIFICATION OF THE HYDROGEN.

The hydrogen was prepared in the familiar zinc amalgam-platinum cell with eight per cent. hydrochloric acid as the electrolyte. This type of cell has been found to deliver very pure hydrogen in numerous atomic weight determinations in the Harvard laboratories. Merck's purest zinc bars were etched with hydrochloric acid, washed and immersed in mercury, which had been washed in mercurous nitrate and redistilled in air and in hydrogen. The amalgam formed the bottom

[1] PHYS. REV., 5, 311, 1915.

layer in a two-liter ground-glass stoppered Wolff bottle (*A*, Fig. 1) electrical connection being made through a tube extending to the bottom of the generator. The cathode was a sheet of carefully cleaned platinum about 100 square centimeters in area which had been coated with a deposit of platinum black by the electrolysis of a solution of chlor-platinic acid. The hydrochloric acid was prepared by distillation of a twenty per cent. solution of the purest commercial acid and subsequent dilution of the purer fractions of the distillate with distilled water.

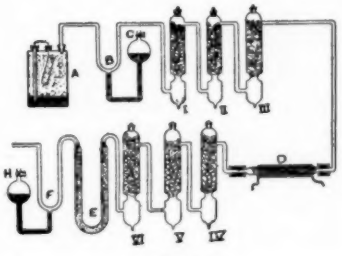

Fig. 1.

In order to prevent contamination of the hydrogen by organic materials, we avoided the use of stop-cock grease throughout. The stoppers of the generator and of the purifying towers were surrounded by short lengths of wide rubber tubing, which permitted the entire stopper to be covered with mercury. This arrangement proved to be sufficiently gas-tight. In place of stop-cocks, we substituted the U-tubes *B* and *F* (Fig. 1) filled with mercury, which could be opened by applying suction at *C* and *H*. The hydrogen from the generator passed first through three Emmerling towers filled with lumps of potassium hydroxide which had been fused with a little potassium permangate to remove organic matter. This freed the gas from acid spray, chlorine, carbon dioxide and a large part of its water vapor. Air, which had been dissolved in the acid solution, was next removed by passing the hydrogen through a hard glass tube filled with clean asbestos fibres which had been soaked in chlorplatinic acid solution and ignited to impregnate them with platinum black. The tube was wound with nichrome ribbon covered with asbestos and maintained at a red heat by an electric current. The joints between the hard glass and the soft glass of the rest of the system were ground to a close fit and surrounded by a jacket of glass filled with mercury. This again gave a gas-tight joint without the use of grease. (See *D* in Fig. 1.) The gas was again dried in three towers of potassium hydroxide lumps and passed finally through the U-tube *E*, about eighteen inches in length and filled with phosphorus pentoxide, which removed the remaining water vapor.

The hydrogen after this treatment could have been contaminated only with nitrogen and the rare gases which might have been dissolved in the acid of the generator. To remove even these as far as possible, we exhausted the whole system by means of a water aspirator to very

close to the vapor pressure of the acid solution. Hydrogen was then generated until the pressure reached atmospheric value. After three repetitions of this exhaustion, the entire system was swept out by its own hydrogen for forty hours before the commencement of the actual experiment.

As a further precaution against some unknown impurity in this hydrogen, we made a few experiments with hydrogen derived from the electrolysis of a weak solution of potassium hydroxide containing a little barium hydroxide to remove carbonate. The solution was in a cylindrical vessel and a wide ring of heavy platinum wire formed the anode. Within this hung a smaller glass cylinder tapering at the top and sealed to a glass tube which in turn was sealed to the U-tube in place of the Wolff bottle, *A*. A strip of platinum gauze sealed into the inner cylinder formed the cathode. The cylinder extended ten inches below the level of the cathode and anode in order to prevent contamination by the oxygen liberated at the anode. This hydrogen was purified exactly as in the first case, except that the system could not be exhausted.

We used still another variety of hydrogen, namely the electrolytic hydrogen as supplied compressed in tanks by the International Oxygen Company. A short piece of rubber tubing connected the tank to the purifying system used before. The accumulation of water in the fourth Emmerling tower in this case revealed some impurity of oxygen.

THE CHEMICAL ACTIVITY IMPARTED BY THE RAYS.

In the first experiments undertaken we attempted to measure the contraction in volume which should ensue, if H_2 is converted into H_3. A definite though small contraction appeared. On account of the size of the effect a study of the chemical properties of the gas by some dynamic method seemed more promising. In point of fact, the chemical properties as revealed by the dynamic method are important in their bearing on the observed volume change, so that the latter will be described after the reactions.

In the first experiment a bulb of about 4 cm. diameter was coated on the interior with a thin layer of sulphur by distilling flowers of sulphur into it in a vacuum. The bulb was similar to the bulb *B* of Fig. 2, and the bulb *A*, containing the radium emanation, was similarly placed at the center of *B*. Pure hydrogen entered through a side tube and after passing slowly through the field of radiation passed out through a glass tube, which dipped into a weak solution of lead acetate, and which held in its mouth a strip of filter paper kept moistened by the solution. A block of lead was so placed that only a minute quantity of gamma

radiation from the emanation could reach the test paper or the acetate solution. Wourtzel has reported the decomposition of hydrogen sulphide by the rays, and inasmuch as ammonia, water and hydrobromic acid have been seen to be both decomposed and synthesized by the rays, it is perhaps not surprising that the lead acetate paper showed a decided blackening after the hydrogen had passed over it during one night.

This is the only reaction of a heterogeneous nature that has been reported as produced by the rays. The question arises as to whether the reaction is a consequence of the activation of the sulphur surface, or of the hydrogen, or is an effect of the actual firing of the hydrogen molecules into the sulphur by the bombardment of the alpha particles. The last mechanism is not very probable because the rays penetrate readily through hydrogen and comparatively few hydrogen molecules are given high velocities. The question is capable of ready answer. In the following experiment the bulb in which the hydrogen was radiated did not contain sulphur, and the hydrogen after emerging from it passed through a short tube containing redistilled flowers of sulphur and thence over a lead acetate paper (see Fig. 2). A block of lead protected the sulphur from the direct action of the rays. The paper was blackened even more rapidly than in the preceding experiment. Repetition of both these experiments with no change except the withdrawal of the emanation produced no blackening. Without the sulphur there is also no effect on the acetate paper.

Since the black coloration of the test paper can be due only to sulfide the evidence is conclusive that the sulphur is being reduced by some more or less stable compound, which is a stronger reducing agent than ordinary hydrogen, and which becomes active after having been intensely bombarded by alpha rays. If this compound is an impurity in the hydrogen it is difficult to imagine its nature. The reduction effect was obtained equally well with the three quite different sources of hydrogen. A number of tests were made in which the hydrogen, in addition to the above described rigorous purification, passed through a glass spiral two feet in length immersed in liquid air. Precisely the same results followed. The only gases which could have survived this purification are helium, neon, argon and nitrogen, and the acquirement of reducing properties by any of these is harder to understand than the activation of hydrogen itself. Finally whatever impurity may have been present was so very dilute that the minute fraction of it that could have been acted upon by the rays would be unable to produce effects of the magnitude observed. The evidence points unmistakably to an abnormal activity on the part of the hydrogen itself.

This does not necessarily mean that a reactive molecule is being formed. The hydrogen is subjected to a very intense ionization by the alpha rays, and though the mobility of the gaseous hydrogen ion is high, large numbers of ions undoubtedly are not yet recombined when they reach the sulphur. It is entirely possible that the observed reactivity may be due to these charged particles in the same manner that chemical activity is the distinguishing mark of the hydrogen ion in solution. To test this point we inserted a plug of glass wool between the ionization bulb and the sulphur tube. Glass wool is exceedingly efficient in filtering out ions, but in this case it had no effect on the result. This experiment indicated the presence of a real modification of hydrogen, which is chemically active. It cannot, however, be the same as Langmuir's hydrogen because the latter not only cannot exist in the presence of any considerable number of other hydrogen molecules but it is condensed completely by glass, especially in the form of wool.

To eliminate further the possibility that ions produce the observed effects a tube was inserted between the ionization bulb and the sulphur tube into which were sealed two platinum rods about four centimeters in length and a centimeter apart on opposite sides of the tube (see *F* in Fig. 2). These were connected respectively to the terminals of a battery composed of two hundred very small cadmium cells, and were therefore at a difference of potential somewhat over two hundred volts. The mobility of the hydrogen ion in hydrogen is nine cms. per sec. per volt per cm., and during the time allowed for the hydrogen to pass through this tube all the ions must have been swept out of the stream of gas. Nevertheless the paper was blackened precisely as before. Later some tests were made using the large storage battery in the Jefferson Physical Laboratory, but even the application of two thousand volts produced no diminution in the chemical activity. The chemical activity, therefore, cannot be due to the presence of ions.

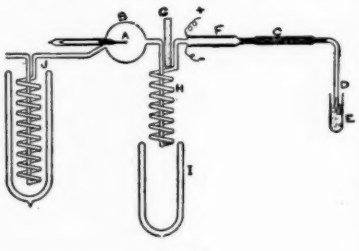

Fig. 2.

We are dealing, then, with a more or less stable, reactive molecule. Judging from the properties of Langmuir's hydrogen, which certainly consists of free atoms, this new form cannot be monatomic. In Langmuir's experiments the free atoms as they were liberated from solution in the tungsten or platinum filament deposited at once on the glass wall of the evacuated bulb and formed there a thin layer. It was not possible for him to obtain large quantities because the formation of

more free atoms resulted only in their recombination with others on the glass to form diatomic molecules. He did not obtain the atomic form at all unless the pressure was so low that the atoms were able to pass from the filament to the wall without encountering other molecules. On the other hand, the modification we observed is fairly stable at atmospheric pressure and it passes readily through a long plug of closely packed glass wool—facts which exclude the possibility of its being monatomic. The molecule is therefore polyatomic and larger than H_2. It will be seen that all subsequent experimental data bears out this interpretation.

An instance in point is the stability of this modification. Ozone reverts spontaneously to oxygen at the rate of about 0.6 per cent. per minute, and a polyatomic form of hydrogen would be expected to have a similar, though perhaps somewhat greater, instability. We noted early in the research that reducing the velocity of the stream of hydrogen diminished the effect on the sulphur. If more than one minute elapsed between the exposure of the hydrogen to the rays and its contact with the sulphur, results were unsatisfactory. A few special experiments established the fact that doubling this interval reduced by much more than one half the chemical action.

The fact that this modification of hydrogen has a much higher boiling point than that of ordinary hydrogen, being condensed even at the temperature of liquid air, accords with the conception of a polyatomic molecule. Fig. 2 illustrates the apparatus designed to investigate this point. The hydrogen on emerging from the purifying system as pictured in Fig. 1 passed through the glass spiral *J*, two feet in length, which was kept completely immersed in liquid air throughout the experiment in order to remove any condensible impurity. Passing into the bulb *B*, the hydrogen was exposed to the alpha rays from the emanation contained in the small bulb *A*. It passed then through the spiral *H*, through an electrostatic field of four hundred volts per centimeter in *F*, through a short plug of glass wool, then over the flowers of sulphur in the tube *C*, and finally over the strip of filter paper, *D*, moistened with lead acetate in *E*. Natural size photographs of the test papers resulting in this experiment are shown in Fig. 3. Since it is not possible to reproduce test papers from all the experiments carried out, those here presented may be taken as typical. A coloration as feeble as that in (*b*) was never accepted as positive evidence. (*a*) and (*c*) however are very typical tests. The parabolic trace near the center of the strips corresponds with the mouth of the glass tube where the hydrogen formed bubbles and had a longer time to react with the lead salt. The test

(*a*) was obtained by passing the hydrogen through the apparatus just as indicated in Fig. 2, for six hours. At the end of that time another paper was inserted and the Dewar bulb, *I*, filled with liquid air, was raised to cover the spiral, *H*, through which the hydrogen passed after exposure to the rays but before contact with the sulphur. Nothing else was altered. In six hours the test appeared as shown in (*b*). With the Dewar bulb, *I*, lowered again a six hours' run produced the test (*c*). Especial care was taken to maintain the velocity of the hydrogen stream at twenty cubic centimeters per minute throughout the eighteen hours of the experiment. Although there is a barely perceptible blackening of the second paper, the active constituent of the hydrogen has evidently been removed by the low temperature. If this is a true condensation the boiling points of H_2 and of this hydrogen are at least seventy degrees apart, and probably more. It must be noted, however, that adsorption of gases is much increased at low temperatures and that consequently the effect observed may be due to an increased selective adsorption of the active gas by the glass walls of the spiral, though this is hardly probable in view of the great excess of H_2 always present. One other interpretation of the disappearance of the activity is that the low temperature hastens the decomposition of the larger molecule into H_2, but this is inconsistent with the conceptions of kinetics.

Fig. 3a.

Fig. 3b.

Fig. 3c.

Fig. 3.

In this test — as in every other—a blank run made without the emanation produced no blackening. *G* is a block of lead five millimeters in thickness which prevented the beta and most of the gamma radiation from reaching the sulphur or the test paper.

An attempt was made to obtain further information about the stability of the active gas by interposing between the ionization bulb and the sulphur tube a device for heating the gas to about 500° C. This consisted of 40 cm. of fine platinum wire wound spirally on a quartz rod supported by little quartz feet within a tube of soft glass sealed to the rest of the apparatus. The terminals of the platinum wire were sealed into this outer tube and connected through a rheostat with a 110-volt circuit, and thus heated to dull redness. No information could be obtained from this apparatus, however, because it was not found possible

within the available period of one minute to heat the hydrogen to the temperature of the platinum wire and thereafter cool it again to a temperature at which the ordinary hydrogen, unaided by the rays, no longer attacked the sulphur. No blank tests could be obtained that did not show some slight action of the ordinary heated hydrogen on the sulphur.

A number of other reactions, besides the formation of hydrogen sulphide, were studied.

On substituting a tube of red phosphorus for the sulphur tube phosphine was formed even more readily than the sulphide had been. A test paper moistened with silver nitrate solution (and kept in the dark) blackened considerably in the course of three hours. Here again a blank test showed no action without the rays. It is interesting to note that Langmuir's active hydrogen is completely destroyed when a little phosphorus vapor is admitted into the evacuated bulb.

Powdered arsenic was also readily reduced to arsine, but this reaction is slower than the two preceding, an exposure of about twelve hours being necessary for a good test. The Gutzeit test was employed. The filter paper strips were moistened with nearly saturated mercuric chloride solution. The coloration obtained was the usual brown shading into yellow, both turning deep black when dipped into a solution of ammonia.

An interesting criterion of the reactivity of this hydrogen lies in the possibility of its attacking metallic bismuth to form the hydride. The formation of BiH_3 by this new hydrogen would have indicated a greater reducing power than that possessed by nascent hydrogen. When pulverized bismuth was placed in the contact tube a test lasting twenty-four hours produced no mirror in a glass capillary tube kept at about 250° by a luminous gas flame. No deposit of any kind was noted, so that the bismuth does not appear to be reduced. This form, then, is not more active than nascent hydrogen.

The new hydrogen attacks mercury.[1] This was discovered quite by accident, when, in an experiment on the volume effect, a few droplets of mercury were spattered against the interior wall of the ionization bulb. After a day of radiation we noticed that the droplets were covered with a crust of minute yellow crystals. Their form could not be determined with accuracy even under a magnification of 900 diameters. Thereupon a wide glass tube which served as a sort of trough for about six cubic centimeters of mercury was sealed in place of the contact tube so that the hydrogen passed directly over the surface of the mercury. In the course of two hours a faint yellowish scum appeared that on allowing the hydrogen to pass over night, increased to a golden-yellow,

[1] As does Sir J. J. Thomson's X_3.

wrinkled film which, as it became progressively thinner on the side removed from the ionization bulb, showed two distinct series of interference spectra. Not enough of the yellow substance could be obtained from the deposit for an analysis. This is regrettable, because the result of the test, unlike the others that have been mentioned, might have been due to the presence of oxygen in the hydrogen and the formation of ozone. In view of the preparation and purification of the hydrogen the presence of oxygen is extremely improbable, and such as was present should,—on the basis of Scheuer's work,—have combined rapidly with the hydrogen to form water. That so notable a quantity of oxide should have been formed is hardly possible. The yellow substance was insoluble in water and resisted attack by weak alkalis, but dissolved in HCl and HNO_3. On standing for a week it decomposed, leaving a dirty grey deposit which on heating collected into droplets and distilled off, *i. e.*, mercury. The experiment was repeated several times, but in the course of two weeks all the yellow color regularly disappeared. This is excellent evidence that the crystals are a hydride of mercury, since such conduct would be expected of that substance while the oxide is very stable in air. Two similar fractions of the yellow substance were sealed in glass tubes, one in an atmosphere of oxygen, the other in hydrogen, but no difference could be noted in their rates of decomposition, except that both changed rather more slowly than samples kept in the open air. When gently warmed the yellow crystals broke up rapidly to give tiny drops of mercury.

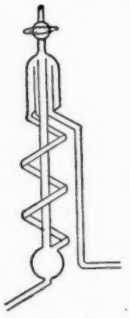

Fig. 4.

This hydrogen reduced neutral potassium permangate solution to manganese dioxide. The absorption tube (Fig. 4) was used for this test and for all other tests involving the reduction of substances in solution. It is designed for the absorption in a minimal quantity of reagent of a small quantity of a gas which is diluted with a large excess of an inert gas. The gas enters through the tube at the left and bubbles up through the reagent passing through the spiral also, in the form of bubbles. It escapes at the top while the reagent which has been driven up returns through the vertical tube. This gives very efficient absorption by small quantities of solution. The device, however, was not necessary in the case of potassium permangate reduction because the reaction is so rapid that the manganese dioxide deposited as a brown ring around the bottom of the tube through which the gas entered the absorber. Here, as above, a blank test without the emanation gave a negative result.

The same absorption tube was used in an attempt to reduce two organic dyestuffs in water solution. Neither methyl violet nor indigo carmine, however, were bleached by several days' passage of the hydrogen. The one, indigo carmine, involves the reduction of a ketone group to a carbinol, the other, methyl violet, the reduction of a quinone grouping. Both of these can be effected with nascent hydrogen, so that this form of the gas would seem to be less active than the nascent. The fact that the substances are in solution, however, may interfere with the reaction. In a separate test the hydrogen bubbled through water between the radiation and its contact with the sulphur. This reduced the amount of sulphide only slightly, and water itself, therefore, seems not to affect the active gas.

Mention may here be made of an experiment (to be described later) in which a mixture of nitrogen and hydrogen was exposed to the rays. Although a contraction in volume resulted, a test of the gases with Nessler's reagent revealed only a small amount of ammonia. The reaction between nitrogen and the active hydrogen thus seems to be very slow.

A review of the facts thus far established shows that we are dealing with a modification of hydrogen which is more active than the ordinary form but less active than the nascent or Langmuir's monatomic states, —properties which demand a polyatomic molecule larger than H_2. In accord with this also are the physical instability and the boiling point. In many respects the new gas is related to hydrogen as ozone is to oxygen, but no method could be devised for determining its molecular weight.

Change of Volume Experiments.

Fig. 5 represents the arrangement of the apparatus to detect the change in volume due to the rays. Before the experiment the water-bath, *C*, was not in place and the bulb *A* was connected by glass tubing with the hydrogen generator and purifier while the bulb *B* was connected through a small mercury trap with the open air. The mercury in the U-tube was drawn into *E* by applying suction at *G* and the two bulbs thereby connected. Pure hydrogen was swept through at a rate of about fifteen cubic centimeters a minute for over twenty-four hours. The tube leading from *B* dipped into a beaker of mercury through which the hydrogen bubbled before reaching the open air. This was to prevent the diffusion of air into the bulbs. When thoroughly swept out and filled with pure hydrogen the bulbs were sealed off as shown in the diagram. The water bath was then put in place and filled in order to equalize the temperature in the two bulbs. This bath was constructed

of a shallow crystallizing dish through the bottom of which three holes were drilled for the passage of the three tubes. The dish was partly filled with mercury and into this was set a tall cylindrical bottomless beaker. Water was poured into this to completely cover the two bulbs. Stirring was effected by a stream of air bubbles rising through the bath.

After standing at a fairly constant temperature for four or five hours the mercury was allowed to rise in the U-tube, D–X, by opening the stopcock F. H is a trap to prevent access of air into the U-tube from the bulb, E. Since the bulbs B and A have nearly the same volume the levels of the mercury in D and X are nearly the same. Both positions are marked on scales attached to the outside of the tubes. The tubes D and X are capillary tubes with a bore of half a millimeter, so that violent tapping is needed to determine the true level of the mercury in each arm. Once the level was thus determined the mercury could be raised or lowered and accurately reset on the marks.

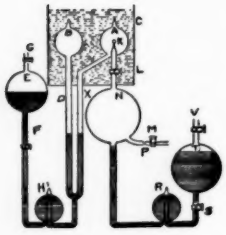

Fig. 5.

The emanation is then introduced into the small bulb, K. For this purpose the emanation is compressed at the radium laboratory into a fine capillary tube about two centimeters in length. This is inserted into the bore of the stopcock, M, in such a way that it projects on both sides. A sealed connection is then made at M with a Gaede rotary mercury pump. The stopcocks L and M are open and the bulbs N and K are exhausted until no difference in level was exhibited by a MacLeod gauge with a magnification of one thousand. The pump is then sealed off from the apparatus shown in the diagram, leaving the bulbs evacuated. The stopcock, M, is then turned and the fine tube containing the emanation breaks, allowing the emanation to enter the bulb N. The stopcock, M, is then sealed off at the constriction, P, and by opening the cock, S, the mercury rises in N driving the emanation into K. When the mercury has reached the neck of the bulb K the stopcock L is closed. This is necessary to avoid changes in level of the mercury due to the large thermal expansion and contraction of the mercury in the bulb N. With L closed these are applied to the air space in the trap, R.

In every case, the introduction of the emanation into K produced a contraction in volume A, indicated by a rise of the mercury in the capillary tube, X. The change in volume opposes and overbalances the expansion due to the heating effect of the emanation.

The contraction in volume did not appear immediately. The pressure change seldom amounted to a millimeter at the end of an hour. At

the end of three hours the pressure usually had fallen three millimeters, and did not exceed this limit even after fifteen hours. Such a pressure change involves a loss of 3/760 or 1/250 in volume, *i. e.*, 0.4 per cent. The bulb, *A*, contained about five cubic centimeters so that the actual contraction amounted to 0.02 cubic centimeter.

The interpretation of the observed contraction is not quite clear, and the phenomenon will be the object of further experimentation. The change in volume appears to be rather larger than one would expect from the number of ions produced by the alpha rays. On the other hand, the effect may be due to some chemical reaction such as that between the hydrogen and the mercury in the tube *DX*.

An interesting point now remains to be investigated, namely, whether the active hydrogen is produced directly by the actual bombardment of the atoms, or whether it may not be due to a breaking down of the clusters of atoms which form around the charged ions.

In an attempt to decide this question, we performed the following experiment. Hoping to be able to remove a large fraction of the ions before the clusters could form around them, we ionized the hydrogen in a very strong electrostatic field. Fig. 6 represents the ionizing chamber in the apparatus. The purified hydrogen entered at *D*. *CC* represents a cylinder of sheet platinum 15 cm. long and 4 cm. in diameter. The platinum rod *B* lies along the axis of the cylinder and close to the emanation bulb *A*. A large storage battery was attached to *B* and *C*, and produced a difference of potential of 2,000 volts between them. After passing between *B* and *C*, the hydrogen flowed through *E* into the sulphur tube.

Fig. 6.

The electric field had no appreciable effect on the result. The sulphide paper appeared as black with as without the field.

If the field had destroyed or diminished the action perceptibly, it would have been possible to draw some definite conclusions as to the rôle played by the clusters. As no effect was observed, however, the experiment must be regarded as negative and no conclusions can be drawn from it, either one way or the other. Thus the mechanism of the formation of the active molecules needs further investigation.

CONCLUSIONS.

It appears from the above described experiments that intense bombardment by alpha rays produces in the purest hydrogen we could obtain a certain capacity for entering into chemical reactions, which ordinary

hydrogen at ordinary temperatures does not possess. For instance, the radiated hydrogen combines directly with sulphur to form hydrogen sulfide, with phosphorus to form phosphine, with arsenic to form arsine, etc. It also reacts with mercury, and reduces neutral potassium permanganate solution to manganese dioxide, etc.

This acquired chemical reactivity cannot be ascribed to the direct action of the hydrogen ions, for the passage of the hydrogen through glass wool and a strong electrostatic field (either of which would remove the ions) does not destroy the acquired property of the gas.

The chemical activity may be due to the formation of H_3 by the alpha rays. Certain characteristics of the active gas seem to point in this direction. We have not obtained, however, conclusive proof of the existence of H_3.

Experiments designed to discover whether the formation of the active gas takes place during the actual bombardment by the alpha particles, or subsequently, during the formation or disintegration of ionic clusters turned out inconclusive.

The active modification can be removed from the hydrogen by passing it through a tube immersed in liquid air.

A diminution of volume takes place in the hydrogen when it is bombarded by the rays. Experiments are in progress designed to discover whether this is a primary action, or is due to some secondary chemical reaction.

The active modification of hydrogen is not very stable, its life being measured in minutes.

HARVARD UNIVERSITY.

COMPARATIVE STUDIES OF MAGNETIC PHENOMENA. VIII.

A STUDY OF THE JOULE AND WIEDEMANN MAGNETOSTRICTIVE EFFECTS IN THE SAME SPECIMENS OF NICKEL.[1]

BY S. R. WILLIAMS.

THE photographic method, employed in former papers,[2] for recording the changes in length produced in steel rods and tubes by a magnetic field (Joule effect), showed that small variations might easily be overlooked by the ordinary telescope and scale method of observation, because the latter process does not admit of a continuous record for all field strengths from zero upwards. In the case of one steel rod a very slight initial lengthening occurred and it was only by means of the continuous photographic record that it was detected. As will be shown in this paper this mode of observing the changes in length in nickel rods when subjected to a longitudinal magnetic field also enabled one to pick out details which might otherwise have gone unnoticed.

Two nickel rods, numbered 5 and 6, each 80 cm. long and 0.397 cm. and 0.318 cm. in diameter respectively, were employed in this investigation. Chemical analysis showed only very slight traces of iron present. The change in length (Joule effect) and the twist (Wiedemann effect) was observed in the manner described in the papers mentioned above. Observations were taken on the rods in the condition in which they left the manufacturer, because in this work it was a question of the comparison of magnetic phenomena on the same specimens. Heat treatments and effects of stresses will be studied later. In the Wiedemann effect a rod is magnetized circularly by passing a current through it lengthwise while simultaneously a longitudinal field is applied. These two fields superimposed upon each other give resultant lines of magnetization in the rod which are helical, as shown in Fig. 1. In the Joule effect changes in length occur along the lines of magnetization. This led Maxwell[3] to regard the Wiedemann effect as a special case of the Joule effect, because if changes in length do occur along the helices a twist will result in the rod just as is found in the Wiedemann effect. One

[1] Presented at the Cleveland Meeting of the Physical Society, December 30, 1912.

[2] PHYS. REV., Vol. 34, p. 258, 1912; Amer. Jour. Sci., Vol. 36, p. 555, 1913.

[3] Maxwell, Elec. and Mag., Vol. 2, p. 87, 2 ed., 1881.

difference, however, seems to have been overlooked by Maxwell and other observers, viz., that in the Wiedemann effect the direction of the lines of magnetization is changing and in the Joule effect it is not. In observing the Wiedemann effect it is customary to apply a constant circular field, C, Fig. 1, first, and then a longitudinal field, H, which increases from zero upwards. If one of these components, C or H, Fig. 1, varies then the direction of the resultant field also varies. The larger H becomes, C remaining constant, the more nearly ϕ, the angle between H and the resultant field S, becomes equal to zero, and the direction of the resultant field, S, more nearly coincides with the impressed field H. This change in direction of the resultant field in the Wiedemann effect is, in my opinion, very closely associated with the fact that the maximum twist in this effect occurs at lower values of H than does the maximum elongation in the Joule effect for the same specimens of iron and steel.[1] (See also Fig. 2.)

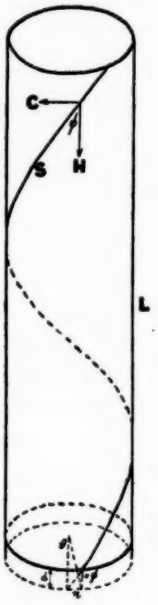

Fig. 1.

From Fig. 1 it may be seen that S, the length of the spiral which forms the direction of the resultant field, is equal to the length of the rod, L, multiplied by the secant of the angle ϕ. For a spiral on the surface of the rod,

$$S = L \sec \phi. \qquad (1)$$

If change in length takes place along this spiral, then it is evident that for small values of H the spiral will be very long, since ϕ is almost 90°. For this long spiral it would not take a large coefficient of magnetic extension with which to multiply S in order to obtain a comparatively large twist and it would be very possible that by the time H had assumed a value where the coefficient of magnetic extension was a maximum that the value of S would have fallen off so that their product would be less than at some previous value of H. This would mean a maximum twist in the Wiedemann effect at smaller values of H than where the maximum elongation in the Joule effect occurs. Due to hysteresis the lines of magnetization in the rod will not follow the lines of force applied to the rod, but will lag[2] and therefore ϕ in Fig. 1 for the lines of magnetization will always be larger than ϕ for the lines of the magnetizing force. A similar line of reasoning will show that for nickel we should get a maximum of twist in the Wiedemann effect although there is no corresponding maxi-

[1] PHYS. REV., Vol. 32, p. 281, 1911.

[2] Ewing, Mag. Ind. in Iron, paragraph 140, and note, p. 238.

mum elongation in the Joule effect. Apparently there is no way in which, apriori, the real length of the spiral of magnetization may be accurately obtained. Suppose, however, that there were no lag, and that we were dealing with an extremely thin walled tube in Fig. 1, instead of a solid rod, or a thick walled tube, then we can get a relation between the Joule and Wiedemann effects if the latter is a special case of the first as Maxwell suggested. Multiplying S by J, the coefficient of magnetic change in length, we will get the expression

$$SJ = JL \sec \phi, \tag{2}$$

which is the total amount of displacement the lower end of the spiral takes in a direction along the spiral. The component of this displacement along the length of the rod produces a change in length, d, Fig. 1, while the component, n, normal to this, produces a twist in the tube. The latter will be equal to

$$(JL \sec \phi) \sin \phi = JL \tan \phi, \tag{3}$$

where

$$\tan \phi = C/H,$$

$$\frac{JL \tan \phi}{r} = \theta, \tag{4}$$

the angle of twist which the lower end of the tube will experience due to the Wiedemann effect, where r is the radius of the tube.

For certain specimens of rather thick walled steel tubes, this equation seems to show qualitative relations very well. This is illustrated in Fig. 2 for a steel tube, B, used in previous investigations,[1] the values of JL, curve L, θ, curve T, and θ/JL, curve A, are plotted with respect to H. The curve for θ/JL is qualitatively what one might expect from the relation $c = H \tan \phi$, for $r\theta/JL = c/H = \tan \phi$. However when we carry out the same curves for a steel tube, designated as C in the paper first referred to, this simple relation breaks down at moderately high fields,

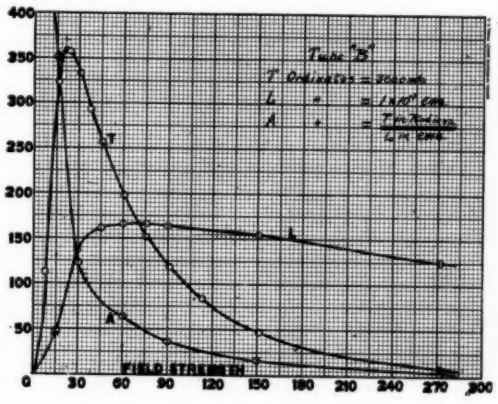

Fig. 2.

[1] PHYS. REV., Vol. 32, p. 281, 1911.

for experimentally we find θ a negative value when J is still positive. This must mean that other factors have entered to mask the simple relation suggested by Maxwell. A change in the orientation of the elementary magnets with the change in the direction of the field might be a possible factor. Here again is a very good illustration of the great complexity with which we have to deal in trying to analyze magnetic phenomena. Any complete analysis seems almost hopeless at times. The publication of the results of investigation on magnetic phenomena should contain very complete details of the modus operandi in securing the data, for only as we know these minutiae of procedure may we make any interpretations of the results that will mean anything. As a general illustration, the magnetic induction of a substance like iron depends upon many factors, such as temperature, stress, extraneous fields, etc., and unless we know thoroughly the past history of that specimen, and how it has been treated, it is hopeless to attempt to compare any results with those obtained by another investigator who has used another specimen which most probably has had still another past history. Only by a comparative study on the same specimens may we hope for progressive results.

As has been indicated, observations on the Wiedemann effect may be made by applying a constant circular field first and then varying the longitudinal field, or a constant longitudinal field may be applied to the rod first and then the circular field varied from zero upwards. If we take the value of the twist for the first case at definite magnitudes of the circular and longitudinal fields, and compare it with the twist for the same magnitudes of circular and longitudinal fields, in the second case we find they are not the same.[1] This difference is to be found largely, I think, in this lag between the direction of magnetization and the magnetizing force.

In one of the papers referred to, the fact was pointed out that in demagnetizing steel and nickel rods, particularly nickel, by means of a decreasing alternating field sent through the magnetizing coil that the specimens were always left in a magnetic condition such that the magnetization was always directed downward in the rods since they were vertically suspended. This pointed to the probability of the elementary magnets in the ferromagnetic substances settling down under the influence of the vertical component of the earth's magnetic field after they had been shaken up by the demagnetizing process. We have an analogous case in an iron rod which becomes magnetic by percussion when placed parallel to the earth's magnetic field. Ordinarily pounding a piece of iron demagnetizes it, especially if the rod is not in a magnetic

[1] Honda and Nagaoka, Phil. Mag., pp. 62, 63, Figs. 11 and 13, Vol. 4, 1902.

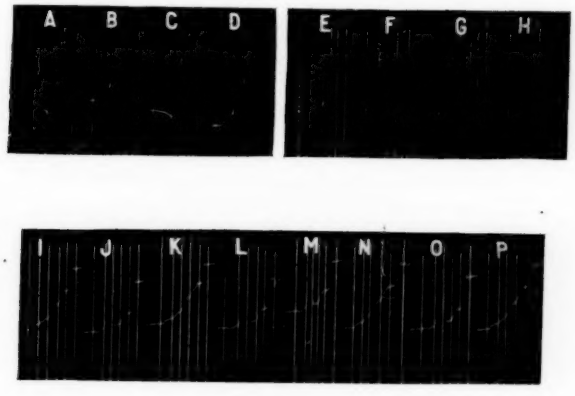

Fig. 3.

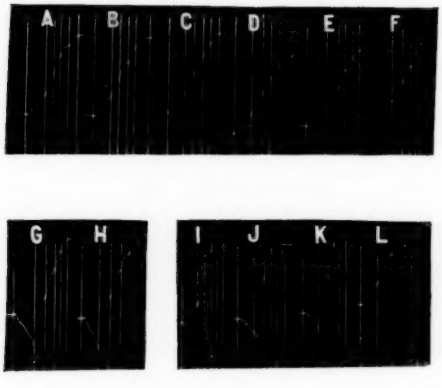

Fig. 4.

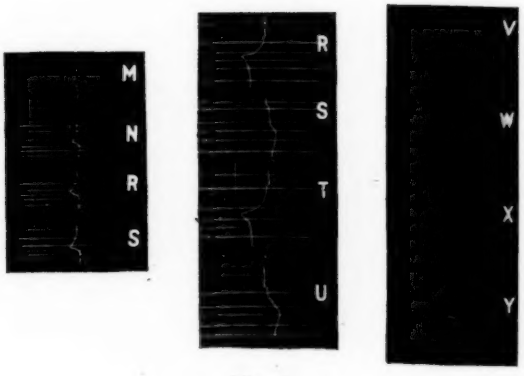

Fig. 5.

S. R. WILLIAMS.

field or is normal to it. In order to make sure of this point a series of experiments was carried out in which various intensities of auxiliary fields were applied to the specimens while they were being demagnetized. The results were very conclusive. If an auxiliary field was applied to the vertical rods in such a way that it was directed upward and its intensity was greater than the vertical component of the earth's magnetic field, then when the rod was demagnetized by a decreasing alternating field in the presence of this auxiliary field the rod would *always* be found magnetized upward instead of downward, as is the case when demagnetized in the earth's field as the only auxiliary field. The presence of these auxiliary fields plays a very important role in the magnetostrictive effects and perhaps most of all in the Joule effect, being especially pronounced in the case of nickel which appears to have its elementary magnets very easily displaced if we may interpret magnetostrictive effects as due to the behavior of the elementary magnets. Ewing and Cowan[1] make note of the fact that "it was only when the earth's magnetic field was exactly balanced that this process gave complete demagnetization." The presence of residual magnetism in the specimen of nickel was an exceedingly sensitive method for determining the auxiliary field necessary to balance the vertical component of the earth's field.

Inasmuch as the changes in length due to a magnetic field could be registered photographically, a further study of these auxiliary fields was made by investigating what kind of changes in length occurred when auxiliary fields other than the earth's field were present during the process of magnetizing the rods. In Figs. 3–6 are shown various photographs taken under different conditions of auxiliary fields. In all cases the graphs may be thought of as moving from the readers right to left behind the lower end of the suspended rod which traces its motion on the film as the field H varies in value. When the trace moves toward the top of the graph there is a shortening of the rod and when the trace is directed downward the rod is elongating.

In A, B, C and D, Fig. 3, is shown the effect of the earth's magnetic field as an auxiliary field upon the nickel rod No. 5. A is for a field in the solenoid which is directed upward and opposed to the vertical component of the earth's field. It will be noticed that there is an initial lengthening followed by a contraction just as is found in steel. Graph B shows the change in length when the field in the magnetizing coil is directed downward, *i. e.*, in the same direction as the vertical component of the earth's field. In this case there is no initial lengthening, the rod contracts from the start. C and D are repetitions of A and B respectively

[1] Ewing and Cowan, Phil. Trans. Roy. Soc. London, p. 326, Vol. 179, 1888.

and show what happens however often the magnetizations are repeated. Before each graph *A*, *B*, *C* and *D*, the rods were demagnetized by a decreasing A.C. field, 60 cycles per second. In each case, however, when the magnetizing force of the solenoid was opposed to the vertical component of the earth's field, there an initial lengthening occurred for nickel, as we find it in steel also.

In Fig. 4, graphs *A*, *B*, *C*, *D*, *E* and *F*, have been taken without demagnetization previous to each record, and each graph was repeated with the magnetizing force of the solenoid in the same direction. *A*, *B* and *C* are with the field up while *D*, *E* and *F* are with the field down. *A* was preceded by a field which was in the same direction as *A*, and *D* also succeeded a field in the same direction as *D*. It is to be kept in mind here that the auxiliary fields present are the earth's field and the remanent field of the rod, the latter evidently being the predominant one as shown by a comparison of *A*, *B*, *C*, *D*, *E* and *F* of Fig. 4 with *A*, *B*, *C* and *D* of Fig. 3. In *G* and *H*, Fig. 4, is shown the effect of reversing the field, first up and then down, without demagnetization before each graph. This again shows the predominance of the remanent field of the rod. Graph *G* was preceded by a field in the opposite direction, *i. e.*, a field similar to *H*.

In order to produce other auxiliary fields a single layer of insulated wire was wound over the whole length of the magnetizing coil. By means of this auxiliary coil magnetic fields of various intensities and directions could be imposed on the rod while the magnetizing force of the main solenoid was being varied. In graphs *I*, *J*, *K* and *L*, Fig. 4, is shown the effect of an auxiliary field produced by the additional coil and of such a magnitude that it was about three times that of the vertical component of the earth's field, 2.18 gauss. In graphs *I* and *J* the auxiliary field is directed upwards while in *K* and *L* this field is reversed. *I* and *K* are for fields in the main coil which are directed upwards while *J* and *L* are downward. Here again it will be seen that whenever the auxiliary field is opposed to that of the magnetizing field of the main coil, that then we get an initial lengthening in nickel. Demagnetization occurred before each graph here also. Finally in graphs *E*, *F*, *G* and *H*, Fig. 3, are shown the changes in length when the vertical component of the earth's field is just annulled. In this case there is no initial lengthening but a decrease in length for all field strengths. Demagnetization occurred before each graph in this set.

In like manner the nickel rod No. 6 was studied and found to be very similar. In fact, rods 5 and 6 came the nearest to being alike magnetically of any two specimens I have ever found. This study of these two rods

has been concerned only with small field strengths, because the magnetic behavior for these fields is of more interest from the standpoint of what is happening inside of the specimens when they are magnetized, than for higher fields. It will be noticed that in all of the graphs for this paper there are six vertical lines to each graph. These are to indicate certain field strengths as the field in the main solenoid was varied from zero upward. The six field strengths thus marked off are: 0, 8.34, 16.67, 25.01, 33.35, 41.68 gauss, respectively. The amount of deflection for each particular field strength will be the distance from a base line passing through the position for zero field to the various points of intersection of the curve and the different vertical lines. These points, when plotted, give exceptionally smooth curves, as shown in previous work.[1] The fact that the zero points for the various graphs on the same film do not lie on a horizontal line simply means that the camera height was readjusted from time to time. This was necessary, because in the demagnetization process, the mirror was sometimes displaced. It does not mean that in the demagnetization the rods did not return to initial conditions. Careful tests found them returning to initial conditions.

Substances possessing an initial lengthening as steel does in the Joule effect also show a "Villari[2] reversal point." There is an intimate relation between these two phenomena. Most of the investigators[3] have not found a "Villari reversal point" in nickel. Heydweiler,[4] however, found such a reversal point in nickel. This present investigation would seem to indicate that the presence of the auxiliary fields, either due to temporary or permanent magnetization, might have something to do with the presence or absence of the "Villari reversal point." In a subsequent paper will be shown how a "Villari reversal point" may be found in nickel and how it may not.

Having shown that it was possible to get an initial lengthening in nickel by the presence of either a remanent magnetic field in the rod itself or by an auxiliary field outside of the rod it was of interest to study the effect of these auxiliary fields upon substances like steel which do show an initial lengthening. In graphs *I*, *J*, *K*, *L*, *M*, *N*, *O* and *P*, Fig. 3, are shown the effects of an auxiliary field upon a steel rod, described as No. 2 in previous papers.[5] In *I*, *J*, *K* and *L* the rod is in an auxiliary field of 70.85 gauss and which is directed upward. This field was kept on continuously while *I*, *J*, *K* and *L* were run off. Demagnetization occurred

[1] PHYS. REV., Vol. 32, p. 293, 1911.

[2] Thomson, Application of Dynamics to Phys. and Chem., pp. 41–59.

[3] Ewing, Mag. Ind. in Iron and Other Metals, pp. 199 and 224.

[4] Heydweiler, Wied. Annal., Vol. 52, p. 288, 1894.

[5] PHYS. REV., Vol. 34, p. 261, Apr., 1912.

before each group. *I* and *K* are for fields up in the main solenoid while *J* and *L* are for fields downward. Graphs *M*, *N*, *O* and *P* are similar to *I*, *J*, *K* and *L*, only the auxiliary field is now directed downward. *M* and *O* are for fields directed upward and *N* and *P* for fields downward in the main coil. Graphs were made, but not shown here, in which the change in length of steel rods was studied when, without demagnetization, the main field was applied alternately first in one direction and then in the other. Very little effect was found due to remanent magnetism. The earth's field also plays a negligible role in the case of steel. It will be seen, however, that it is possible to obtain a curve for steel which shows a shortening for all field strengths in the main coil just as a normal nickel specimen would, the condition being that the direction of the field in the main coil is the same as that of the auxiliary field. This last amounts to a study of change in length of a steel rod after it has reached the point of maximum elongation and consequently will shorten for all field strengths which might thereafter be applied to it. I have just shown, however, that for nickel we get the same effects from auxiliary fields outside of the rod as from inside auxiliary fields due to remanent magnetism, stresses, etc. This is saying that due to causes inherent in the specimen we might have even a steel rod behaving very much as a normal nickel rod, *i. e.*, shortening for all field strengths. In fact, rod no. 1, described in a former paper,[1] was almost in this condition and only by the greatest care could the initial lengthening be detected. We have seen in the graphs already shown that nickel can be made to behave either normally or like steel in its change of length due to a magnetic field. It seems probable, therefore, that by obtaining certain initial conditions in the rods it would be possible to obtain the same type of change in length for all ferromagnetic substances when subjected to a magnetic field.

In a paper[2] describing a model of the elementary magnet I pointed out that a model could be made to exhibit all of the various types of changes in length which we find in the Joule effect in steel, nickel, cobalt, etc., and that the type of change in length depended upon the intrinsic field of the elementary magnet and its initial orientation in the field imposed upon it. In the photographs which have just been shown it has been made clear that the type of change in length for the various substances depended upon the character of the auxiliary fields present. These might be either a field due to remanent magnetism or one produced by an auxiliary coil or any other cause. In other words, these auxiliary fields

[1] PHYS. REV., Vol. 34, p. 261, Apr., 1912.
[2] PHYS. REV., Vol. 34, p. 40, Jan., 1912.

condition the initial orientation of the elementary magnets in the specimen and so the type of change in length. We may now ask why under normal conditions is the change in length in steel different from that in nickel, cobalt, or the Heusler alloys, etc. It would seem to the writer that the above experiments indicate the possibility of the intrinsic fields of the elementary magnets themselves being sufficient to give conditions which shall determine the initial orientation of the elementary magnets. As these intrinsic fields are different for different substances, different initial conditions will be given and so various types of changes in length will occur as we actually find them doing. I have shown that in the case of rods the initial orientation might be greatly influenced by rolling or drawing the specimens. In the case of steel, for instance, the elementary magnets will line themselves up in their own magnetic fields in a definite way and under the same conditions of previous heat treatments, states of strain, etc., there will always occur the same type of change in length. For a given mechanical property there is always associated a definite magnetic property.[1] This type of change in length we can alter, however, by heat[2] treatment, by stresses,[3] and, as has just been shown, by other auxiliary fields. In nickel or some other magnetic substance the fields of the elementary magnets will be different and therefore the alignment of the elementary magnets in their position of equilibrium will be different from that of steel and so a different Joule effect. This is just an extension of the idea of Ewing[4] concerning the mutual effect of the elementary magnets upon each other.

To return once more to the comparison of the Joule and Wiedemann effects. In Fig. 5, *R*, *S*, *T*, *U*, *V*, *W*, *X* and *Y* are shown the twists produced in the nickel rod no. 5, when subjected to a circular field due to a current of three amperes flowing through it and with a longitudinal field varying from zero upward. An auxiliary field was applied to annul the vertical component of the earth's field, hence the graphs in Fig. 5 are to be compared with *E*, *F*, *G* and *H* in Fig. 4, in which the Joule effect is studied under similar conditions of auxiliary fields.

The graphs for the Wiedemann effect show that even with the earth's magnetic field compensated the twist to right and left with reversal of the main field is not symmetrical. This is undoubtedly caused by the special effect of twist due to a longitudinal field, attention to which was called in a former paper,[5] and which is brought about by the structure of the rod being set in a permanent twist in the drawing or rolling process.

[1] Journal of Cleveland Engineering Soc., Jan., 1917, p. 183.

[2] Nagaoka and Honda, Phil. Mag., p. 51, Vol. 4, 1902.

[3] Honda and Shimizu, Phil. Mag., p. 342, Vol. 4, 1902.

[4] Ewing, Mag. Ind. in Iron, 171, p. 299.

[5] Amer. Jour. Sci., Vol. 36, p. 555, 1913.

The films for Fig. 5 are to be thought of as moving upward behind a horizontal slit on which a spot of light is thrown from a mirror attached to the rod. As the rod twists, the spot of light will trace on the moving film the curves as shown. If the twist is toward the left edge of film, it means that the lower end of the rod is twisted clockwise, as viewed from the upper end of the rod. Graphs *R*, *S*, *T* and *U* are for the conditions that a current of 3 amperes flows upward in the rod while alternately a field up and then down is applied by the main coil. *R* and *T* are for fields directed downward and *S* and *U* for fields directed upward. Graphs *V*, *W*, *X* and *Y* have a current of three amperes flowing downward in the rod, while *V* and *X* are for the magnetizing force upward and *W* and *Y* for the main field downward. Demagnetization occurred before each graph.

These photographs of the Joule and Wiedemann effects again show that in the Wiedemann effect there is a maximum twist for which there is no corresponding maximum elongation in the Joule effect, the reason for which has already been given.

Inasmuch as the graphs showing the twist due to a longitudinal field in the paper just cited were taken without the precaution of compensating for the vertical component of the earth's field, graphs are herewith shown in which this precaution was taken. In *M*, *N*, *R* and *S*, Fig. 5, is shown a cycle of twists for varying field strengths. *M* and *R* are for fields directed upward while *N* and *S* show the twist when the magnetizing force is directed downward. Lines of twist in the structure of the rod, when viewed from the upper end, is like a right-handed screw. A comparison of *M*, *N*, *R* and *S* in Fig. 5, with *R*, *S*, *T* and *U* in the same figure will quickly disclose the relation which this latter effect has with the Wiedemann effect.

The solenoid used in this work was a new one and has been described in a recent paper.[1]

SUMMARY.

1. This paper confirms the viewpoint that primarily the Wiedemann effect is a special case of the Joule, but that one condition prevails in the former which does not in the latter; viz., there is a constantly changing direction of the resultant field imposed. This condition gives rise to several variants already noted.

2. There has been offered in this paper an explanation why the maximum twist in steel for the Widemann effect comes at lower field strengths than does the maximum elongation in the Joule effect. In a paper by Knott,[2] he speaks of this as an inexplicable fact.

[1] Jour. Frank. Inst., Sept., 1916, Vol. 182, p. 353.

[2] Knott, Trans. Roy. Soc. Edin., Vol. 39, p. 377, 1890.

3. The importance of considering the effects of auxiliary fields upon the magnetostrictive effects has been brought out. In the case of iron, the earth's field as an auxiliary field has very little influence on the magnetostrictive effects as compared with those in nickel.

4. A possible explanation of why the magnetostrictive effects vary in different substances has been presented.

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OSCILLATORY SPARK DISCHARGES BETWEEN UNLIKE METALS.

BY D. L. RICH.

INTRODUCTION.

IT is known by physicists that there are some twenty factors affecting the production of an oscillatory spark discharge; furthermore, with a few exceptions, there is general agreement as to the part each one of these factors plays. One of the exceptions noted is the effect of the electrode material itself, and that particular phase of the subject forms the basis of this paper.

In view of the very great amount of work that has been done in connection with the electric spark, the effect of the electrode material is very rarely mentioned. In practically all research work on spark discharges the spark has been formed between electrodes of like material, so that opportunities for observing the effect of dissimilar materials have been in general absent. Considering the extensive literature on the oscillatory spark discharge, the lack of experimental data for sparks between electrodes of unlike material is surprising. On the other hand, the effect of the electrode material on the electric arc, both D.C. and A.C., and the behavior of what are known as crystal rectifiers, have been subjects of wide investigation in recent years, and the well-known results therein determined would naturally lead one to believe that the electrode material is not a negligible factor in any electric discharge.

PREVIOUS WORK ON THIS PROBLEM.

One of the earliest investigators of the effect of the electrode material was Righi.[1] He found no difference in the sparking potential in the case of C, Bi, Zn, Sn, Pb and Cu. In 1878, De La Rue and Muller,[2] in addition to their work on the effect of the shape of the electrodes, used their 10,000-cell silver chloride battery to produce sparks between similarly shaped electrodes of unlike material, Cu, Ag, Pt, Mg, Zn, Al, brass and steel. They also found no difference, except in the case of aluminum, from which sparks could be drawn apparently a little more easily. In 1892, Peace[3]

[1] Righi, Nuovo Cimento, 16, p. 97, 1876.
[2] De La Rue and Muller, Phil. Trans., Part 1, p. 55, 1878.
[3] Peace, Proc. Soc. Lond., 52, p. 109, 1892.

worked with Cu, Zn and brass electrodes. His method was to apply a storage battery to two spark gaps connected in parallel. These spark gaps were set at unequal lengths, and enclosed in separate receivers from which the air could be exhausted; then by changing the gas pressure the sparks were shifted from one gap to the other. No variation produced by interchanging the electrode materials was observed. In 1903, Carr[1] measured the breakdown potential difference for brass, Fe, Zn and Al. He likewise found no difference.

When the spark gap is exceedingly short, as in the case of the coherer, the material undoubtedly affects the discharge. Guthe[2] was the first to point this out, showing in 1901 that the cohering effect between electrodes of unlike material takes place at a lower voltage in one direction than in the reverse direction. Hobbs,[3] using like electrodes and very short spark-lengths (two to six wave-lengths of light) claims that the metallic ions take part in the discharge, with the result that the material of which the electrode is composed exerts an important influence on the spark potential. Almy[4] attempts to connect cathode fall with spark potential. To quote him, "The fact that different metals show marked difference in the so-called cathode fall obviously leads to the inference that spark potentials must to a certain extent depend on the material of the electrode used." Later he says, "In air the cathode fall of the different metals differs so little that it hardly seemed probable a difference in spark potentials would be detected." His experimental work was done almost entirely with hydrogen as the gas in which the electrodes were immersed. He used a storage battery to furnish the voltage, and a Weston voltmeter to measure it. In hydrogen he finds fairly consistent differences due solely to the material of the electrodes. In air the only variation in sparking potential that he mentions is in the case of Pt-Al electrodes, the $Pt^{-}Al^{+}$ discharge requiring eight volts more than the $Pt^{+}Al^{-}$ discharge.

The work of Schuster and Hemsalech,[5] followed by that of Milner[6] and of Royds,[7] throws much light on the behavior of metallic ions in the spark gap. These men photographed the spark on a rapidly revolving film, allowing the light to pass through a spectroscope placed between the spark gap and the film. The appearance of the photographed lines enabled

[1] Carr, Phil. Trans., A, 201, p. 419, 1903.
[2] Guthe, Annalen der Physik, 4, p. 762, 1901.
[3] Hobbs, Phil. Mag., 10, p. 619, 1905.
[4] Almy, Univ. of Nebraska Studies, Vol. 6, No. 4, 1910.
[5] Schuster and Hemsalech, Phil. Trans., A, 193, p. 189, 1899.
[6] Milner, Phil. Trans., A, 209, p. 71, 1909.
[7] Royds, Phil. Mag., 19, p. 285, 1910.

them not only to identify the metallic vapors present in the spark, but also to compute the velocities with which these vapors traveled out into the spark gap from each electrode. Their results show that the different metal vapors travel with unequal velocities. Since their work was mainly the determination of ionic velocities they were not concerned with the critical sparking potential, nor with rectification effects. It is however only a logical probability that if the metal ions travel with unequal velocities these same ions are liberated from the electrodes with unequal facility, and therefore the spark might start more readily from some metals than from others; in other words, the measurements of Schuster and Hemsalech rather support the idea that rectification effects due to electrode material do exist.

THE PROBLEM.

If there is a rectification effect of this nature, it should manifest itself when an alternating electromotive force of sufficient magnitude is applied to unlike electrodes. And the behavior of the spark discharge is probably best studied by photographing the spark gap while the discharge is taking place.

Our problem then is really this: *Apply an alternating electromotive force to an oscillatory circuit containing a spark gap made of electrodes mechanically alike but chemically different and determine by photographing the spark whether or not the oscillatory discharge starts as readily when one electrode is anode as when the other is anode.* During one of the series of half-cycles, say that series consisting of the first, third, fifth, seventh, etc., half-cycles, one of the electrodes will be initially an anode; while in the other alternate series, consisting of the second, fourth, sixth, etc., half-cycles, this same electrode will be initially the cathode.

To photograph the spark gap in air at ordinary atmospheric pressure, three principal methods are available: (*a*) To insert either a rotating mirror or a rotating lens between the spark gap and the stationary sensitized surface of the camera. Feddersen, and Trowbridge, for example, used the rotating mirror, while Boyd used a series of rotating lenses. (*b*) To separate the otherwise superimposed oscillations by blowing the sparks from the narrow to the wide end of a V-shaped spark gap by means of a powerful blast of air. Klingelfuss was the first to use this method. (*c*) To receive the image of the spark on a rapidly revolving plate or film. Pierce, and Lodge and Glazebrook used a revolving plate, while Schuster and Hemsalech used a revolving film.

The second method was discarded as undesirable, and throughout this work there has been used a combination of the first and the third methods

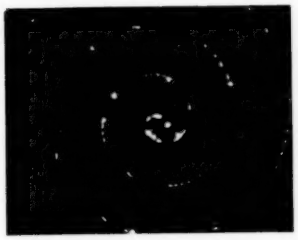

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 5.

Fig. 6.

D. L. RICH.

outlined above, the photographic lens being moved with rather slow velocity, and the photographic film or plate with a much higher velocity.

First Method Used—Plate Camera.

In order to observe the relative number of spark trains per half-cycle no excessive speed of the photographic surface is necessary. For this the following method was found satisfactory. An ordinary glass plate negative, held in its customary plate holder which in turn was clamped centrally on the end of the shaft of a small motor, and at right angles to the shaft, so that the plate could be turned at a fairly high speed in its own plane, was the arrangement used for moving the photographic surface. In order to prevent the superposition of images the lens of the camera was swung slowly across in front of the plate and parallel to it, so that the successive spark trains traced out a spiral on the plate.

To produce these sparks a spark gap, an inductive resistance, and a condenser were connected in series, and then the condenser put directly across the secondary of a rather leaky high voltage transformer whose primary was connected to 110-volt 60-cycle mains.

Figs. 1, 2 and 3 are reproductions of photos secured in this way. Each spot represents not a single spark but a complete train of sparks, the speed of rotation not being sufficiently great to separate the individual oscillations. The groups of spark trains correspond to the half-cycles of the exciting primary current. The asymmetry of the spark trains per half-cycle is very plainly evident, every second half-cycle containing many trains, and the alternate half-cycles fewer trains. In Fig. 1 is a half-cycle (marked "0") that produced no spark trains whatsoever. In Fig. 2 several alternate half-cycles trail off into a tail, indicating that the oscillatory discharge degenerated into an ordinary arc discharge. To test this, the capacity and the inductance were disconnected, and Fig. 3 is the appearance of the resulting arc.

Interpretation and Predictions.

Figs. 1, 2 and 3 are photographs taken when the electrode materials were copper and iron. The asymmetry of the spark trains per half-cycle indicates that there is a rectification effect present in the oscillatory discharge between two electrodes of dissimilar material. Probably if the critical voltage were secured (a difficult task, but not impossible) spark trains would be produced only on alternate half-cycles, the others being entirely suppressed. Even if this critical voltage were not used, but instead a voltage somewhat higher than the critical, rectification effects when present would manifest themselves in at least three ways:

1. *In the Relative Number of Spark Trains per Half-cycle.*—If we assume that the sparks start more easily at one electrode than at the other, we are led immediately to the conclusion that the sparks must start more readily on one half-cycle than on another; that one set of alternate half-cycles will produce more spark trains than the other alternate set. The following diagram (Fig. 4), it is reasonable to suppose, might represent what our assumption leads us to expect. Suppose the electrodes are Cu and Fe, and that the first half-cycle occurs when Fe is initially positive, and the second half-cycle when the electrode Fe is initially negative; and suppose further that we assume that the spark starts the more readily when Fe is negative than it does when Cu is negative. This amounts to the same as assuming that the sparking potential, or the difference of potential necessary to initiate a spark, is relatively high on the $Cu^{-}Fe^{+}$ half-cycles and relatively low on the $Cu^{+}Fe^{-}$ half-cycles. The potential builds up along the curve *AB* until it reaches the sparking potential *CD* at the point *E*. Then a discharge takes place, either unidirectional or oscillatory as the case may be, with the result that the potential difference is reduced to a magnitude less than that necessary to maintain the discharge (not necessarily reduced to zero, however). The voltage then builds up again, let us say along some such line as *FG*, and the process repeats itself until finally the curve reaches *H* and no further discharge takes place until the potential difference builds up in the opposite sense in the next half-cycle, with Fe initially negative. Owing to the relatively high potential necessary to initiate a spark, only a relatively small number of trains will be produced in this $Cu^{-}Fe^{+}$ half-cycle.

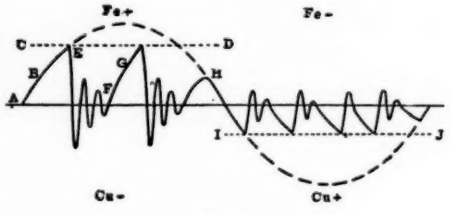

Fig. 4.

During the next half-cycle, if the sparking potential *IJ* is small, the discharges will have a chance to begin *earlier* in the half-cycle; after the falling off of the potential due to the discharge, the potential can build up again to the necessary sparking magnitude *more quickly*; and the sparks can start and last *later* in the half-cycle; *all three* of these factors tend to produce *more discharges* in this $Cu^{+}Fe^{-}$ half-cycle than in the preceding $Cu^{-}Fe^{+}$ half-cycle.

2. *In the Relative Number of Individual Oscillation Sparks per Train.*—When a spark does occur at the higher sparking potential, this spark might reasonably be expected to be of a more violent nature than a spark produced at a lower sparking potential. If more violent, not only would

the condenser be more strongly charged in the opposite sense, but there would also be more ions produced in the spark gap, with the result that the spark gap resistance would be decreased. Both the stronger charge and the lowered resistance would lead one to expect that the oscillations following the initial spark would be more numerous. The large initial charge and the smaller damping decrement would each tend to prolong the duration of the wave train.

3. *In the Relative Number of Spark Trains Containing an Even Number, or an Odd Number, of Individual Oscillation Sparks.*—So far as the material affects matters, if the initial spark in any train starts with ease, the third, fifth, etc. (the *odd* sparks), in that same train, since they start from the same electrode, should also start with ease, with greater ease than the second, fourth, etc. (the *even* sparks), which originate at the other electrode, from which the spark starts with difficulty. It would naturally be expected that any spark train would stop with an easy spark, *i. e.*, at the beginning of a spark difficult to start. That is, if the initial spark of any train starts easily, that particular spark train might be expected to contain an *odd* number of sparks. Likewise, the train whose first spark originates at an electrode from which the spark starts with difficulty should in general contain an *even* number of individual sparks.

But in addition to the material of the electrodes there are at least two other factors (even with the electrodes mechanically and chemically alike) that probably have an influence on the oddness or evenness of the number of sparks per train. The primary current is changing while the secondary discharge is taking place. The flux change in the secondary due to this slowly changing low frequency primary current, combined with the flux change in the secondary due to the rapidly changing high frequency secondary current, since these two changes are in the same sense during half the sparks and in opposite sense during the other half, would probably produce an asymmetry that would favor one set of sparks always whether the electrodes were of the same material or not.

Also, the ionization produced in the spark gap is a function of the velocity of the ions, which velocity is in turn dependent on the potential at which the ions were emitted,—a high potential difference producing a high velocity and therefore a low capacity for ionization. So considering the three factors, and not knowing their relative magnitudes it is impossible to predict which spark trains will contain an even number of individual oscillation sparks, and which an odd number.

Reasons for Changing to a Film Camera.

To investigate the above matters it became necessary to rearrange both the camera and the oscillatory circuit. The first method used, and

the photographs secured, samples of which are shown above, are satisfactory to determine the relative number of spark trains per half-cycle; but to obtain photographs showing individual oscillation sparks the photographic surface must be made to move at a very much higher rate, and the period of the oscillatory discharge must be lengthened to secure a much lower frequency.

To lower the frequency a larger inductance coil and a larger condenser were built. The inductive resistance was a circular coil a meter in diameter and a meter high, and consisted of about a hundred turns of no. 12 coppered iron wire wound on a rough wooden frame. Its low frequency resistance was 6.5 ohms, and its low frequency inductance 25 millihenrys. The condenser was made of 48 large panes of ordinary window glass, each pane shellacked, coated on both sides to within five centimeters of the edge with tin foil, then given two more coats of shellac. The panes were mounted in a wooden frame with air insulation. When thoroughly dry the leakage was not excessive, but the absorption was very bad. The low frequency capacity ranged from an eighth to a half microfarad, depending on the duration of the charge and of the discharge.

To increase the speed of the camera the glass plate was abandoned and a film used instead (Eastman extra rapid speed film, about 55 inches long and $2\frac{1}{2}$ inches wide). The film was wrapped around the flat outside rim of a wheel 40 cm. in diameter. This made the total exposed length of the film about 1,260 mm. The wheel was mounted on a motor running 2,000 revolutions per minute, giving a linear velocity to the film of about 42,000 mm. per second. In order to hold the film in position at this rather high speed it was found necessary to bolt the film to the wheel with twelve bolts arranged zigzag around the circumference. By actual measurement of the developed films it was found that this inductance, capacity and film speed resulted in a separation of the individual oscillation sparks to distance of 4.1 mm., a distance amply sufficient for all present purposes.

As before, exposure was made by swinging the lens across the film while the film was rotating at a high speed, so that the spots of light traced out a continuous spiral on the film. The lens was moved by a heavy weight which in falling from ceiling to floor picked up counterbalancing weights so that its speed was kept approximately constant. Further the weight in falling automatically operated a mercury switch so that the spark discharge took place only while the lens was passing in front of the film. By adjustment it was found possible to cause the spiral to trace out twenty complete turns on each film, thus *enabling the spark gap to be kept under continuous observation for over half a second at a time,*

showing the groups of spark trains in over sixty consecutive half-cycles all spread out in a single line photograph over twenty-five thousand millimeters long.

Data Secured from a Typical CuFe Photo.

Half-cycles in Which Fe Was Initially *Negative.*				Half-cycles in Which Fe Was Initially *Positive.*			
Half-cycle.	Number of Spark Trains.	Number of Sparks in Each Train.	Total Number of Sparks.	Half-cycle.	Number of Spark Trains.	Number of Sparks in Each Train.	Total Number of Sparks.
1		Incomplete		2		Incomplete	
3		Incomplete		4		Incomplete	
5	4	5 2 2 2	11	6	3	5 3 3	11
7	7	4 2 2 2 2 2 2	16	8	2	5 3	8
9	2	5 3	8	10	4	4 2 3 3	12
11	6	4 2 2 2 2 2	14	12	2	5 3	8
13	6	4 2 2 2 2 2	14	14	2	5 3	8
15	5	4 2 2 2 3	13	16	3	4 3 3	10
17	5	5 2 2 2 3	14	18	3	5 3 3	11
19	9	4 2 2 2 2 2 2 2 2	20	20	2	5 3	8
21	8	4 2 2 2 2 2 2 2	18	22	4	5 3 3 3	14
23	7	4 2 2 2 2 2 2	16	24	3	5 3 3	11
25	5	4 2 2 2 2	12	26	3	4 3 3	10
27	5	4 1 2 3 2	12	28	3	4 3 3	10
29	4	4 3 2 3	12	30	3	4 3 3	10
31	8	4 2 2 2 2 2 2 2	18	32	4	4 3 2 3	12
33	6	4 2 2 2 2 2	14	34	3	5 3 3	11
35	9	4 2 2 2 2 2 2 2 2	20	36	2	5 3	8
37	8	4 2 2 2 2 2 2 2	18	38	3	5 3 3	11
39	7	4 2 2 2 2 2 2	16	40	3	3 3 3	9
41	5	3 3 2 2 2	12	42	5	3 2 2 2 3	12
43	9	4 2 2 2 2 2 2 2 2	20	44	2	3 3	6
45	7	4 1 2 2 2 2 2	15	46	4	3 3 3 3	12
47	7	3 2 2 2 2 2 2	15	48	3	3 3 3	9
49	7	4 2 2 2 2 2 2	16	50	4	3 3 3 3	12
51	7	4 2 2 2 2 2 2	16	52	2	5 3	8
53	9	4 2 2 2 2 2 2 2 2	20	54	4	4 2 2 3	11
55	8	4 2 2 1 2 2 2 2	17	56	3	3 3 3	9
57	8	4 2 2 2 2 2 2 2	18	58	4	4 2 2 3	11
59	11	2 2 2 2 2 2 2 2 2 2 2	22	60	3	3 3 3	9
61	8	3 2 2 2 2 2 2 2	17	62	4	3 3 3 3	12
63	8	4 2 2 2 2 2 2 2	18	64	4	3 3 3 4	13
65		Incomplete		66	4	3 3 3 3	12
67		Incomplete		68	3	3 3 3	9

To show relative number of spark trains per half-cycle, and also to show relative number of oscillation sparks per train, it is desirable to use a short spark gap, and highly damped oscillations. Fortunately these conditions are the very easiest possible.

A large number of photographs were taken, in an interval extending over two years. Most of the work was done on CuCu and CuFe electrodes in an attempt to settle definitely the point in question with these particular metals. Later electrodes of zinc and bismuth were used in various combinations with each other and with copper and iron. Many different specimens were used, and several different shapes. The sparks were always produced in air at atmospheric pressure. The spark gap was varied in length from 0.1 mm. to 3 or 4 mm., while the lens of the camera was so placed that the image of the spark gap was slightly longer than the spark gap itself.

Figs. 5 and 6 are sections of typical films showing the appearance of the sparks between CuFe electrodes and CuCu electrodes respectively. Owing to the fact that some of the beginning and the ending half-cycles are incomplete on the edges of the films, the number of half-cycles observable in the two series are in general unequal; however, no error is thus introduced as average values are desired, and any number of half-cycles may be averaged.

CuFe Summary.

	Cu^+Fe^-.	Cu^-Fe^+.
Total number of half-cycles observed	30	32
Total number of spark trains	205	101
Average number of spark trains per half-cycle	6.2	3.16
Total number of oscillation sparks	472	327
Average number of oscillation sparks per train	2.3	3.23
Number of trains consisting of 1 spark	3	0
Number of trains consisting of 2 sparks	166	9
Number of trains consisting of 3 sparks	10	71
Number of trains consisting of 4 sparks	23	9
Number of trains consisting of 5 sparks	3	12
Total number of spark trains consisting of an *even* number of sparks	189	18
Total number of trains consisting of an *odd* number of sparks	16	83
Per cent. even	92.2	17.7
Per cent. odd	7.8	82.3

An examination of the CuFe data summary shows that the spark trains on the Cu^+Fe^- half-cycles were almost double the number of trains on the Cu^-Fe^+ half-cycles (6.2 to 3.16); that the number of oscillation sparks per train was over a third larger (2.3 to 3.23) in the Cu^-Fe^+ half-cycles than in the Cu^+Fe^- half-cycles; and that in the Cu^-Fe^+ half-cycles 82 per cent. of the trains contained an *odd* number of sparks, while in the Cu^+Fe^- half-cycles 92 per cent. of the trains contained an *even* number of sparks.

INTERPRETATION.

The relative number of spark trains per half-cycle, and the relative number of sparks per train indicate clearly that the $Cu^{+}Fe^{-}$ discharge takes place more readily than the $Cu^{-}Fe^{+}$ discharge. The fact that an odd number of sparks per train predominates during the $Cu^{-}Fe^{+}$ half-cycles and an even number during the $Cu^{+}Fe^{-}$ half-cycles indicates that the ionizing effect is the predominating influence in determining the evenness or oddness, as the sparks as a rule stop with the higher voltage, higher velocity, lower ionizing discharge.

In contrast with the preceding data, which was secured from a typical series of discharges between electrodes mechanically alike but chemically different, and which show rectification effects attributable solely to electrode material, compare the following set of data, from a characteristic series of discharges between CuCu electrodes.

Summary of Data Secured from a Typical CuCu Photo.

	Odd Half-cycles.	Even Half-cycles.
Total number of half-cycles observed	31	33
Total number of spark trains	63	74
Average number of spark trains per half-cycle	2.03	2.24
Total number of oscillation sparks	250	291
Average number of oscillation sparks per train	3.97	3.93
Number of trains consisting of 1 spark	0	0
Number of trains consisting of 2 sparks	0	0
Number of trains consisting of 3 sparks	10	7
Number of trains consisting of 4 sparks	45	64
Number of trains consisting of 5 sparks	8	3
Number of trains consisting of an *even* number of sparks	45	64
Number of trains consisting of an *odd* number of sparks	18	10
Per cent. even	71.5	86.5
Per cent. odd	28.5	13.5

An examination of the CuCu data summary preceding shows that the average number of spark trains per half-cycle is practically the same in the two series (2.03 to 2.24); that the average number of individual sparks per train is almost identically the same (3.97 to 3.93); and that in both series the spark trains are predominantly of four sparks each. In not one of these three respects is there even any hint of rectification effects. The irregularities which do occur in discharges of this nature are probably due to the conducting variations in the spark gap, possibly caused by air-currents, etc., variations which prevent the absolutely uniform charging of the condenser.

In every photograph, without a single exception, I have found the CuCu discharge to be symmetrical, and the $Cu^{+}Fe^{-}$ discharge to be more easily produced than the $Cu^{-}Fe^{+}$ discharge.

DETERMINATION OF POLARITY.

In order to determine which particular kind of spark should be associated with the $Cu^{-}Fe^{+}$ discharge, and which with the $Cu^{+}Fe^{-}$, the A.C. primary circuit was disconnected and there was substituted a 220-volt D.C. source, through a suitable non-inductive high resistance and a knife switch. The fact that the primary E.M.F. was high, produced a rapid change of flux in the transformer when the switch was closed, and consequently a vivid spark in the secondary circuit; yet the resistance inserted in the primary circuit resulted in less than a volt across the primary coils, so that it was perfectly safe to put an ordinary 250-volt voltmeter directly across the secondary of the high potential transformer, and thus determine definitely and easily the polarity of the spark electrodes at make and at break. The voltmeter behaved as a ballistic galvanometer, and by the direction of its "kick" gave positive evidence concerning the polarity.

The camera film was set in motion, the camera shutter closed except at "make," and a series of make spark photos secured. Then the lens was displaced sideways slightly, the shutter closed except at "break," and a series of break spark photos obtained. The electrodes were then reversed, and the make and the break photos again taken, all on the same film, side by side.

When the primary circuit was closed, a single spark train was expected. As a matter of fact the photographs showed several spark trains for each make, the number varying from four to forty-two, depending on the length of the spark gap. This may be explained as follows:

Suppose the total quantity of electricity flowing into the condenser of the secondary circuit be plotted against time, giving the familiar curve of Fig. 7. A quantity q_1 might be sufficient to charge the condenser to

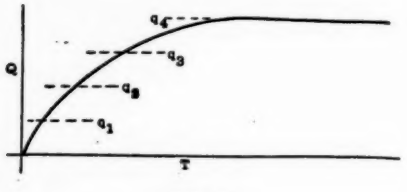

Fig. 7.

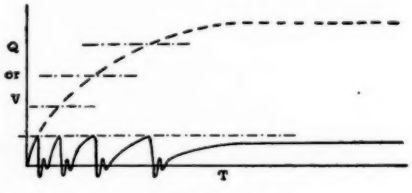

Fig. 8.

the sparking difference of potential, and an oscillatory discharge would then occur. A further quantity $q_2 - q_1$ might again charge the condenser, and another oscillatory discharge ensue; and again a quantity $q_3 - q_2$, and still further $q_4 - q_3$, and so on, might each cause a spark train. The fact that at each make the first spark trains were not only

more intense but also made up of from five to eight oscillation sparks each, while the later spark trains were of less intensity and also of shorter length (2, 3, or 4 oscillation sparks each) supports the above explanation. The curve (Fig. 8) probably represents what took place:

Owing to the arcing effect at the knife switch when the primary circuit was opened, usually only one spark train was observed at "break," and it was usually much fainter than the sparks at "make."

Several films were used in this manner. In every case the photos of the $Cu^{-}Fe^{+}$ discharge consisted of light, narrow, faint spots alternating with heavy, broad, darker spots, and *always beginning with* the fainter spot, as shown in (*a*) Fig. 9; while the $Cu^{+}Fe^{-}$ discharge photo was of similar alternations, but *always beginning with the broad dark spot*, as shown in (*b*), Fig. 9. The metallic vapor liberated in the spark gap when iron was anode always produced the much more intense light effect. On all the photos, whether produced by direct current or alternating current means, the polarity of the electrodes could be identified easily and positively. Furthermore, on the D.C. photos, the $Cu^{+}Fe^{-}$ discharge without exception consisted of an even number of oscillation sparks; while the $Cu^{-}Fe^{+}$ generally, though not always, consisted of an odd number of sparks.

Fig. 9.

When the electrodes were of the same material, for example CuCu, the sparks were always of like character throughout, gradually growing fainter as the amplitude decreased, as shown in (*c*), Fig. 9. Furthermore the number of individual oscillation sparks when the electrodes were alike was predominantly even.

FURTHER RESULTS WITH OTHER ELECTRODE COMBINATIONS.

It next seemed desirable to investigate the behavior of some other metals when used as electrodes, in order to see whether or not there exists a consistent rectification series among conductors in general. The same method was continued, and zinc, bismuth, copper and iron electrodes were used repeatedly in all possible combinations.

Iron-bismuth was one of the first combinations tried. Below is a summary secured from a typical Fe-Bi photo.

An examination of this summary, particularly the relative number of spark trains per half-cycle, and the relative number of oscillation sparks per train, indicates that the discharge can start more readily when iron is negative. Each of the other films of this particular electrode combination indicated the same rectification. Not much reliance, however, can be placed on the relative number of even and odd spark trains.

Iron-Bismuth Summary.

	$Fe^{-}Bi^{+}$.	$Fe^{+}Bi^{-}$.
Total number of half-cycles observed	28	29
Total number of spark trains	146	83
Average number of spark trains per half-cycle	5.21	2.86
Total number of oscillation sparks	218	184
Average number of oscillation sparks per train	1.49	2.21
Number of trains consisting of 1 spark	76	15
Number of trains consisting of 2 sparks	68	35
Number of trains consisting of 3 sparks	2	33
Number of trains consisting of an even number of individual sparks	68	35
Number of trains consisting of an odd number of individual sparks	78	48
Per cent. even	46.5	42.1
Per cent. odd	53.4	57.8

After finding that the spark discharge could be initiated more readily from iron that from either copper or bismuth (always assuming that the discharge is electronic in nature, so that the current flows from anode to cathode), the next step seemed to be the investigation of the copper-bismuth spark gap. Below is a copy of the data secured from a characteristic CuBi film. Note the 3's.

Copper-Bismuth Summary.

	$Cu^{+}Bi^{-}$.	$Cu^{-}Bi^{+}$.
Total number of half-cycles observed	32	32
Total number of spark trains	69	34
Average number of spark trains per half-cycle	2.16	1.06
Total number of oscillation sparks	201	101
Average number of oscillation sparks per train	2.91	2.97
Number of half-cycles producing no spark	1	5
Number of trains consisting of 1 spark	0	0
Number of trains consisting of 2 sparks	7	1
Number of trains consisting of 3 sparks	61	33
Number of trains consisting of 4 sparks	1	0
Number of trains consisting of an even number of individual sparks	8	1
Number of trains consisting of an odd number of individual sparks	61	33
Per cent. even	11.5	3
Per cent. odd	88.4	97

Here again, as in all of this work, the criterion as to rectification lies in the relative number of spark trains per half-cycle. After the spark is once started various extraneous and uncontrollable irregularities lessen the reliability that can be placed on the way in which that particular spark train continues. On the above film, twice as many spark trains originated from the bismuth anode as from the copper anode. And five

times as many failures to produce any discharge whatsoever are charged to the copper anode.

Another combination tried was zinc and iron. The spark when iron is anode is always easily recognized, the light from the spark then apparently being exceedingly rich in actinic rays.

Iron-Zinc Summary.

	Fe^-Zn^+.	Fe^+Zn^-.
Total number of half-cycles observed	31	29
Total number of spark trains	96	41
Average number of spark trains per half-cycle	3.1	1.41
Total number of oscillation sparks	181	115
Average number of oscillation sparks per train	1.88	2.80
Number of trains consisting of 1 spark	46	4
Number of trains consisting of 2 sparks	17	1
Number of trains consisting of 3 sparks	31	35
Number of trains consisting of 4 sparks	2	1
Number of trains consisting of 5 sparks	0	0
Number of trains consisting of an even number of individual sparks	19	2
Number of trains consisting of an odd number of individual sparks	77	39
Per cent. even	19.8	4.9
Per cent. odd	80.1	95.0

Here again the half-cycles in which iron was initially the anode produced considerably more than twice as many spark trains as the other series. In fact, the discharge took place so readily from the iron anode that the condenser could receive only a very small quantity of electricity, so small that a return spark was very frequently impossible, as is shown by the fact that 46 of the trains (48 per cent. of them) were unidirectional, one spark discharges.

One of the most prominent cases of rectification which was observed occurred in connection with a copper-zinc spark gap. The data for this particular gap is inserted here not as a typical case, but as a special case, illustrating the fact that with proper adjustment it is possible to initiate spark trains from one electrode alone. The necessary adjustment probably would be difficult to make, and still more difficult to maintain, but the following data show that it can be done.

Other films in the CuZn spark gap, while not so prominently asymmetrical as this one, always showed a decided preponderance of spark trains initiated during the half-cycles when zinc was anode, indicating that a discharge could start from zinc much more readily than from copper.

An inspection of the foregoing summaries shows that rectification effects manifest themselves prominently in the relative number of trains per half-cycle, and generally in the relative number of sparks per train.

Copper-Zinc Summary.

	$Cu^{-}Zn^{+}$.	$Cu^{+}Zn^{-}$.
Total number of half-cycles observed	32	30
Total number of spark trains	14	143
Average number of spark trains per half-cycle	1.27[1]	4.77
Total number of oscillation sparks	38	253
Average number of oscillation sparks per train	2.71	1.77
Number of half-cycles producing 0 trains	21	0
Number of trains consisting of 1 spark	1	55
Number of trains consisting of 2 sparks	2	72
Number of trains consisting of 3 sparks	11	10
Number of trains consisting of 4 sparks	0	6
Number of trains consisting of an even number of individual sparks	2	78
Number of trains consisting of an odd number of individual sparks	12	65
Per cent. even	14.3	54.5
Per cent. odd	85.7	45.4

Since other factors enter into the cause of oddness or evenness of the number of sparks per train, not so much reliance can be placed on the relative number of odd and even trains.

As a result of the work discussed in this paper the conclusion is reached that rectification effects do exist in oscillatory discharges between the unlike metals used, the order being Fe, Bi, Zn, Cu, a spark being initiated with the greatest facility from iron, and with the greatest difficulty from copper.

More complete data of this nature, involving the various elements which may be used as electrodes, may throw light on the stability of ionic or electronic aggregations or orbits within the atom.

Comparison with a Former Result.

It has already been mentioned that Guthe was the first to suggest that the discharge in the case of the coherer is undoubtedly affected by the material of the electrodes. In an attempt to measure the smallest potential difference necessary to produce coherer action Guthe[2] experimented with many different metals, among which were the same four, Cu, Bi, Fe and Zn, mentioned in this paper. Since in the coherer the two electrodes are either in actual contact or else separated by an exceedingly thin layer or film, the conditions are somewhat different from the ordinary spark gap. Further, the potential difference applied to the coherer was a very slowly changing, and finally constant, statical, battery potential difference; whereas the voltage used in this work was always a rapidly changing, alternating, transformer potential difference. Nevertheless, if the discharge is electronic, either method should yield some

[1] 11 half-cycles only.

[2] Guthe, Ann. d. Physik, 4, p. 762, 1901.

information concerning the facility with which electrons are torn from the anode and fired across the spark gap or the coherer film. Guthe arranges the metals in the order Bi, Fe, Zn, Cu, the series beginning with the easiest and ending with the hardest; *i. e.*, ending with the metal requiring the highest potential difference to produce coherer action. His series differs from the series proposed in this paper only in the relative positions of bismuth and iron.

SUMMARY.

Many photographs of the oscillatory spark discharge between electrodes mechanically alike, but chemically different, were taken, in an attempt to determine whether or not the material of the electrode has any influence on the initiation of the discharge.

Electrodes of copper, iron, zinc and bismuth were used; also both alternating currents and intermittent direct currents were used; in producing the required potential differences.

The interpretation of the relative number of spark trains per half-cycle, the relative number of individual oscillation sparks per train, and the relative number of trains containing odd numbers and even numbers of individual sparks, is given, with reasons for such interpretation.

When the electrodes were alike symmetrical discharges were always found.

When the electrodes were of two unlike metals decided rectification effects were always produced, being very pronounced when copper was one of the electrodes, and most prominent when iron was the other electrode. In other words, the material of the electrodes is not a negligible factor in the initiation of a spark discharge.

If the discharge is electronic, the electrons are emitted from iron more easily than from bismuth or zinc, and much more easily than from copper; they are emitted from bismuth more easily than from zinc or copper; and from zinc more easily than from copper. Arranged in a rectification series, these metals stand

Fe, Bi, Zn, Cu.

The rectification effects seemed marked and consistent throughout. Many and various specimens of metals in various shapes were used all in air at ordinary atmospheric pressure.

In conclusion, my thanks are due to Professor K. E. Guthe, under whose helpful supervision this work was done; and also to Professor N. H. Williams for much good advice during the progress of the work.

UNIVERSITY OF MICHIGAN,
ANN ARBOR, MICHIGAN,
April 1, 1915.

OPTICAL CONSTANTS OF THE BINARY ALLOYS OF SILVER WITH COPPER AND PLATINUM.

BY LOUIS K. OPPITZ.

HISTORICAL INTRODUCTION.

THE first studies in the optical constants of alloys were those of Drude[1] who investigated three alloys: (*a*) one of 18 k. gold alloyed with silver, copper, and a small quantity of iron; (*b*) one of copper-nickel; and (*c*) Wood's alloy. He made no attempt, however, to study any complete series of alloys related according to some well conceived property.

Willi Meier[2] measured the optical constants of Wood's alloy and those of an alloy of gold and silver of equal parts by weight. His main interest was in the study of optical constants for a series of wave lengths which extended into the ultra-violet region.

Bernouilli[3] measured the optical constants of a number of alloys, that form solid solutions; but restricted his examinations to small concentrations, that is to dilute solid solutions. His work includes a study of the optical constants of Ag-Tl, Ag-Sn, Cd-Hg, Cu-Sn and Cu-Ni. The main interest in his work is his method,[4] which consisted of the measurement of the minimum azimuth of restored polarization.

Voigt[5] has criticized the mathematical formula employed by Bernouilli as an illegitimate approximation.

Littleton[6] was the first to study the variation of optical constants for entire alloy series. He investigated the alloy series of Cu-Ni, Fe-Mn, Ni-Fe, Ni-Si, Al-Cu and Cu-Fe. These alloys seem not to have been chosen for the purpose of studying group characteristics.

In 1912, Eckhardt[7] investigated a series of gold-silver alloys. Gold and silver form an unbroken series of solid solutions. The series investigated consisted of ten members of progressively varying compositions. The concentration-refractivity curve of the series is continuous and shows

[1] Drude, Ann. d. Phys., N. F., Vol. 39, 1890, pp. 481–554.
[2] Willi Meier, Ann. d. Phys., Ser. 4, Vol. 31, 1910, pp. 1017–1099.
[3] Bernouilli, Zeitschr. d. Elektro-chem., 15, pp. 646–648.
[4] Ann. d. Phys., Ser. 4, Vol. 29, pp. 585 et seq.
[5] Voigt, Ann. d. Phys., Ser. 4, Vol. 29, 1909, pp. 956 et seq.
[6] Littleton, PHYS. REV., Vol. 32, 1911, pp. 453 et seq.
[7] Eckhardt, Doctor's Thesis, University of Pennsylvania.

a distinct but weak maximum, while the absorptive index curve shows a distinct minimum at about the same concentration. The indices of refraction of nearly all of the gold-silver alloys are higher than those of either component forming the series.

OBJECT, THEORY AND METHOD OF THE PRESENT INVESTIGATION.

The object of the present investigation is a study of the optical constants of two complete series of binary alloys, silver-copper and platinum-silver.

The copper used in the alloys was electrolytic copper, while the silver was 1,000 fine assay silver.

The alloys were approximately of the same size and mass. The masses of the metals constituting the alloys were carefully determined on a chemical balance. The alloys were also weighed after being fused. In no case was there a greater loss due to evaporation than one part in about three hundred. The boiling point of silver is about 1950° C. In order to avoid the loss of silver by evaporation, the platinum was first fused, and the silver was introduced gradually into the melted platinum. The regulus was then carefully stirred by means of a carbon rod and was kept at red heat for several hours, to insure a homogeneous mixture.

The alloys were fused in graphite crucibles in a resistor furnace. They are free from graphite, as is shown by the values of the optical constants of the pure metals. The source of energy was an alternating current passed through a step-down transformer.

POLISHING OF THE MIRRORS.

The method of polishing was approximately that of Drude. After the alloy had cooled it was mounted and a plane face was turned on it in a jeweler's lathe. It was then treated with emery. Fine grades of French emery paper of four degrees of fineness (*i. e.*, 0, 00, 000, 0000) were used. The process of polishing began with the use of the 0 grade that being the coarsest. The specimen was stroked in a definite direction against the emery paper. The emery paper was held on a smooth plate of plane glass. Each mirror required individual treatment. The pressure of the stroke was adapted to the hardness of the particular alloy. The surface of the alloy was stroked so as to give to the scratches a single definite direction. Then the mirror was stroked in a direction at right angles to the scratches imparted to it by the coarsest grade of emery paper, against an emery paper of the next grade of fineness and so on until the finest grade of emergy paper had been used. Each succeeding grade of emery paper thus tended to remove or to render less deep the

scratches introduced by the preceding, and to insure a plane surface. If any scratches remained after the finest emery had been used, recourse was had to a burnishing tool like that used by silversmiths. Much care was exercised to keep the surface of the emery paper free from dust and other forms of contamination.

Drude's criterion for a satisfactory optical surface was used: the azimuths of restored polarization for light parallel and perpendicular to the scratches must be approximately equal. The phase change was found to be invariable for a given angle of incidence so long as the mirror remained free from surface layers.

OPTICAL METHODS.

The source of light was a Bunsen flame colored by means of fused NaCl. This light was filtered though an aqueous solution of $K_2Cr_2O_7$ which rendered the resulting light practically that of the D lines of sodium. The light incident upon the surface to be studied was plane polarized at an azimuth of 45°. This light after reflection became elliptically polarized and was reconverted into plane polarized light by means of a Soleil-Babinet compensator. The azimuth of restored plane polarization was determined by means of an analyzing half-shadow-nicol system. Then the analyzing nicol was set for extinction and the phase change was determined by the use of the compensator. The angle at which the plane polarized light became incident upon the surface of reflection was carefully determined by reading the position of the telescope from the goniometer circle. In order to determine the azimuth of restored polarization, a modified form of the Zehnder[1] half-shadow polarimeter was used. This consisted of the usual analyzing nicol and a movable smoked glass wedge, adjacent to the nicol and moving over a fixed smoked glass wedge. In its original form the polarimeter was made up of an analyzing nicol adjacent to a fixed smoked glass plate. The intensity of the light used for studying the optical properties of the surfaces was found to vary for different angles of incidence and for different optically reflecting surfaces. It was therefore found that relatively large angles of incidence were the most favorable. At suggestion of Dr. Eckhardt, of this laboratory, the fixed smoked glass plate to which reference has been made was replaced by a movable smoked glass wedge, which could be varied so as to change the length of the path traversed by the light passing through it. This rendered it possible to adapt the length of the path to the intensity of the light traversing the polarimeter. This gave half shadow equality through a range varying from 7° to 21°. The determination of the position of

[1] Zehnder, Ann. d. Phys., 26, 1908, pp. 985–1018.

extinction of the analyzing nicol with the polarizer depended upon judging half-shadow equality. Half-shadow equality is most easily judged when the illumination through the analyzing nicol and smoked glass appears homogeneous and intense. Two half-shadow equality positions were viewed, one on each side of the extinction position of the analyzing nicol. Then the analyzing nicol half-shadow device was rotated approximately 180° and two other half-shadow equality positions were found. Thus, there were four readings in all from which to find the extinction position of the nicol. The arithmetical mean of the positions before and after extinction gives the extinction position.

Much practice was necessary for attaining proficiency in the judgment of half-shadow equality. After considerable preliminary practice, the initial step in the experimental work was to determine the optical constants of electrolytic copper. The experimental values obtained for pure copper are as follows:

n	nK	K
.640	2.63	4.10 Drude,
.620	2.57	4.14 L.K.O.

The difference in the two sets of values is probably explainable on the basis that the two specimens of copper used, differed in purity. After determining these optical constants for pure copper, those of nine different alloys of silver-copper, of eight alloys of silver-platinum and pure silver and pure platinum were measured. The entire eleven points of the silver-copper curves (Fig. 3) and the entire ten points of the platinum-silver curves were experimentally determined (Fig. 4).

In the figures, the variation in the composition of the alloys is expressed in terms of the atomic per cent. of copper. The reflecting power was obtained by calculation, and not by direct measurement. No explanation is at present offered for the anomalously high reflecting power of the silver-copper alloy of 4.99 per cent. concentration.

WORKING FORMULÆ.

The well known formulæ of Drude were in the calculation of the optical constants:

$$n^2(1 + K^2) = \tan^2 P \sin^2 \phi \tan^2 \phi. \qquad (1)$$

The atomic per cent. of one component is given by

$$x = \frac{100p}{p + (100 - p)\frac{a}{b}},$$

where p = per cent. by weight of this component, a = its atomic weight and b = the atomic weight of the other component.

$$K = \tan Q \tag{2}$$

$$\tan \Delta = \sin Q \tan 2P \tag{3}$$

$$\cos 2\psi = \cos Q \sin 2P \tag{4}$$

$$R = \frac{n^2(1 + K^2) + 1 - 2n}{n^2(1 + K^2) + 1 + 2n} \tag{5}$$

where

n = the index of refraction,
K = the absorptive index,
Δ = the phase change,
ψ = the azimuth of restored polarization,
R = the reflecting power,
ϕ = the angle of incidence.

EXPERIMENTAL RESULTS.

Silver-Copper Alloys.

Silver and copper form a series of alloys in which there are two limited series of solid solutions, separated by a gap. This gap consists of a series of eutectiferous alloys. As one withdraws from pure silver, silver crystals, *i. e.*, crystal type I. separate out, and this lowers the melting point. At 8.5 per cent. of copper concentration, the solid solutions of silver are saturated, being incapable of taking up any further quantity of copper. After that, the crystals contain varying amounts of silver imbedded in the melt. At 40 per cent., the melt solidifies about the crystals. The saturation point for copper is 96 per cent. Likewise from 100 per cent. copper to 40 per cent., the crystals vary in the amount of copper contained. At 40 per cent. of concentration, the solid solutions are in equilibrium with the melt, and therefore a eutectic mixture is formed. These thermal relationships obtained from Guertler's Metallographie are given in Fig. 1.

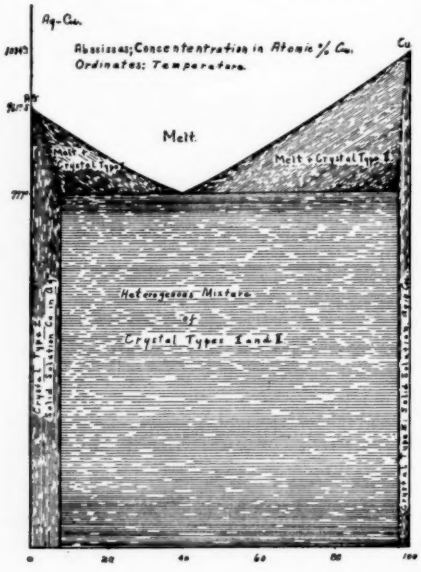

Fig. 1.

The optical constants of these alloys are shown in Table I. while Fig. 3 is a graphical representation of the same.

TABLE I.

Silver-Copper Series.

Wt. Per Cent. of Cu.	Atom. Per Cent. of Cu.	n	K	nK	R
0	0	.202	17.08	3.44	94
3	4.99	.252	11.35	2.86	98.8
6	10.27	.517	6.51	3.31	84.87
10	16.49	.492	7.51	3.69	87.68
30	42.12	.36	6.61	2.40	80.92
50	62.94	.312	7.57	2.37	82.92
72	40.00	.244	13.78	3.36	93.26
80	87.14	.416	7.05	2.93	84.35
90	93.87	.507	5.71	2.90	80.98
95	96.99	.643	5.01	3.22	80.26
100	100.00	.620	4.14	2.57	73.11

The concentration-refractivity curve shows a minimum near the eutectic point, the index of refraction being the lowest here excepting that of pure silver. As the eutectic point is left in either direction, there is an increase in the index of refraction.

The absorptive index-concentration curve shows a relative maximum near eutectic point, but the absorptive index of every alloy is higher than of copper and always lower than of silver.

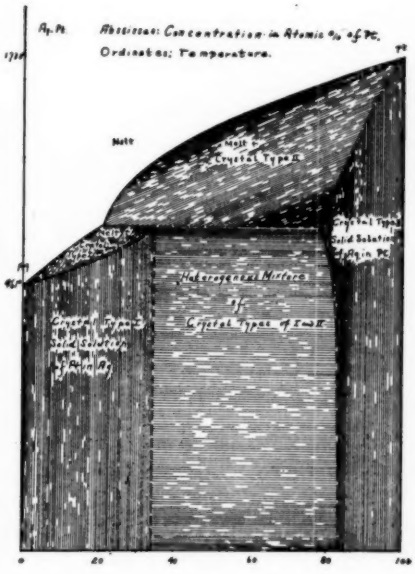
Ag. Pt.
Abscissae: Concentration in Atomic % of Pt.
Ordinates: Temperature.
Melt
Heterogeneous Mixture of Crystal Types of Ag and Pt

Fig. 2.

Platinum-Silver Alloys.

Similarly platinum and silver form two series of solid solutions separated by a gap. This gap consists of a region of heterogeneous mixture of silver and platinum extending from approximately 34.8 per cent. to 83.5 per cent. of platinum concentration. Beyond these points in either direction, we find solid solutions. These relations are found in Fig. 2. This was also obtained from Guertler.

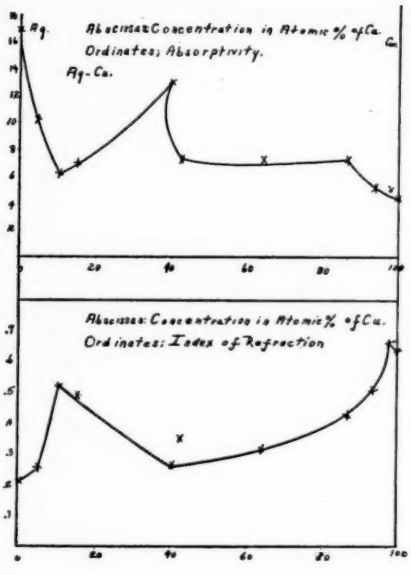

Fig. 3.

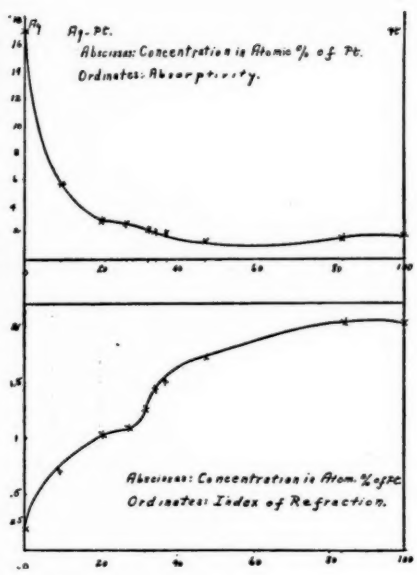
Ag-Pt.
Abscissæ: Concentration in Atomic % of Pt.
Ordinates: Absorptivity.
Abscissæ: Concentration in Atom. % of Pt.
Ordinates: Index of Refraction.

Fig. 4.

The optical constants of these alloys are found in Table II. while their graphical representation is embodied in Fig. 4.

TABLE II.

Platinum-Silver Series.

Wt. Per Cent. of Pt.	Atom. Per Cent. of Pt.	n	K	nK	R	Loss in Mass of Alloy After Fusing.
0	0	.202	17.08	3.44	94%	0.000 gr.
15	8.9	.71	5.92	4.26	86.54	0.035
30	19.18	1.05	3.69	3.91	78.85	0.020
40	26.97	1.13	2.736	3.09	67.95	0.032
45	31.18	1.26	2.42	3.10	65.56	0.000
48	33.83	1.45	2.29	3.33	65.98	0.000
50	35.64	1.57	2.15	3.39	65.27	0.000
62	47.47	1.74	1.82	3.18	60.41	0.000
90	83.39	2.12	1.85	3.95	66.24	0.000
100	100.00	2.03	1.96	3.80	65.61	0.000

Good working surfaces of the platinum-silver alloys were easily obtained.

The concentration refractive index curve shows an unmistakable increase toward pure platinum. The concentration absorptive index curve indicates a very sudden drop from pure silver to the next member of the series. After that the decrease is very gradual. The absorptive index

of pure platinum is slightly lower than that of the solid solutions of crystal type II. in Fig. 2.

In general, for platinum-silver alloys as well as silver-copper alloys when solid solutions are formed, an index of refraction which increases with the concentration indicates a decreasing absorptive index.

A typical sample of the readings (those on the eutectic alloy of silver and copper) is included below:

Sample Series of Observations for Mirror No. 1

Atomic per cent. Cu = 40. *Eutectic Alloy of Silver and Copper.*

Angle of Incidence = 74° 7′.

I. *Scratches Parallel to Plane of Incidence.*

Polarizer at 285° 59′.

28° 10′	47° 20′	204° 45′	230° 30′
25	46 50	205 10	35
10	47 25	204 50	50
20	10	55	40
2 20	15	205 00	40
28 17	47 12	204 56	230 39
Aver. 37° 44′		Aver. 217° 47′	

Polarizer at 195° 59′.

295° 35′	327° 55′	121° 40′	142° 35′
35	328 00	10	45
296 05	327 40	15	10
295 40	50	30	30
40	45	20	30
295 43	327 51	121 23	142 30
Aver. 311° 47′		Aver. 131° 56′	

Polarizer at 105° 59′.

28° 05′	47° 20′	204° 45′	230° 45′
27 55	05	205 05	25
28 15	15	204 55	35
00	25	205 10	40
15	20	00	50
28 06	47 17	204 59	230 39
Aver. 37° 41′		Aver. 217° 49′	

Polarizer at 375° 59′.

296° 05′	328° 05′	121° 25′	142° 15′
295 35	327 40	10	50
296 10	328 00	10	30
295 35	327 45	15	35
296 20	328 15	20	40
295 57	328 15	121 16	142 34
Aver. 311° 57′		Aver. 131° 55′	

$$2\psi = 217° 47′ - 131° 56′ = 85° 51′$$

$$\pi - 2\psi = 311° 47′ - 217° 47′ = 94°$$

II. *Scratches Perpendicular to Plane of Incidence.*

Polarizer at 285° 59′.

28° 10′	46° 50′	205° 00′	230° 30′
15	47 00	204 45	50
25	46 55	50	35
20	47 20	205 10	40
20	25	204 55	35
28 18	47 06	204 56	230 38
Aver. 37° 42′		Aver. 217° 47′	

Polarizer at 195° 59′.

295° 15′	328° 59′	122° 05′	141° 55′
30	327 40	121 30	142 10
20	50	40	30
45	45	15	20
40	55	20	20
295 30	327 50	121 24	142 15
Aver. 311° 40′		Aver. 131° 49′	

Polarizer at 105° 59′.

28° 15′	46° 50′	204° 40′	230° 40′
30	47 00	50	45
20	15	55	35
25	20	205 10	40
2 20	10	00	50
28 22	47 07	204 55	230 42
Aver. 37° 44′		Aver. 217° 48′	

Polarizer at 375° 59′.

295° 20′	327° 35′	121° 55′	142° 05′
40	328 05	25	141 50
35	327 40	30	142 15
50	50	15	25
20	55	40	30
295 33	327 49	121 33	142 13
Aver. 311° 41′		Aver. 131° 53′	

$$2\psi = 217° 47′ - 131° 49′ = 85° 58′$$

Compensator Readings.

Before Extinction.		After Extinction.	
Main Scale.	**Scale.**	**Main Scale.**	**Scale.**
16.00	04	17.00	19
15.75	97		34
16.00	48		47
	14		77
	09		86
Av.....16.00	14	17.00	52

General Average: 16.50, 33 divisions.

SUMMARY OF RESULTS.

1. Near the eutectic point, the index of refraction is lower than that of any other member in the silver-copper series, except that of pure silver, while the absorptive index is a relative maximum for the same concentration.

2. The indices of refraction of the alloys at the saturation points in the two regions of solid solutions for silver-copper are higher than that of the pure metal near these points.

3. From the eutectic point of the silver-copper series, there is a marked increase in the index of refraction in either direction until saturated solid solutions are formed. The absorptive index shows a behavior which is approximately the inverse of that shown by the index of refraction.

4. The reflecting power of a metal of relatively low reflecting power is in general improved by mixing this metal with one of relatively higher reflecting power. This is in agreement with the work of others.

5. Whenever solid solutions are formed an increasing index of refraction indicates a decreasing index of absorption. This is borne out by the studies of both the silver-copper and platinum-silver series.

In conclusion, I wish to record my grateful appreciation to Dr. H. C. Richards for placing at my disposal the facilities of the Randal Morgan Laboratory of Physics. Not only has he shown interest throughout the entire progress of this work but it is to him that I owe my first interest in the subject of optical constants. It is also with pleasure that I acknowledge my indebtedness to Dr. E. A. Eckhardt who has aided me with numerous valuable suggestions in every detail of the work.

THE RANDAL MORGAN LABORATORY OF PHYSICS,
UNIVERSITY OF PENNSYLVANIA.

IONIZATION OF POTASSIUM VAPOR BY ORDINARY LIGHT.

BY J. A. GILBREATH.

THERE has been some doubt as to whether the vapors of the alkali metals are photo-electric under the influence of ordinary light Anderson found that potassium vapor was ionized by ultra-violet light.[1] Hughes criticizes his conclusions and suggests that the photo-electric currents observed by Anderson were not due to the vapor but were surface effects.[2] This investigation, suggested by Dr. Anderson, was undertaken to determine whether or not potassium vapor is ionized by ordinary light.

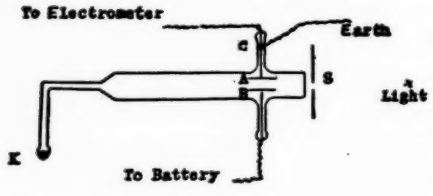

Fig. 1.

A tube with parallel plate electrodes of the type shown in Fig. 1 was used. The tube was of ordinary glass impervious to ultra-violet light. The electrodes were of copper, about 2 cm. wide by 3 cm. long and separated by a space of 1 cm. There was a platinum cylinder fused into the glass at *C* and earthed to prevent conduction over the glass. The solid potassium distilled in vacuo was in bulb *K*. The vacuum at the start was about .005 mm. of mercury. There was a slit at *S* 1 mm. wide through which the light was admitted. The source of light was an arc or a 500-watt nitrogen filled tungsten which was focused by a lens system on the slit. The currents were measured by a quadrant electrometer with a sensibility of 4,000 mm. per volt. When the light and slit were in the position shown in Fig. 2 and so adjusted that the light passed evenly between the electrodes, very little striking either electrode, distinct photo-electric currents were observed when a sufficient E.M.F. was applied at *B*.

With zero potential at *B* no currents were obtained in any case. When a positive potential of 317 volts was applied a current represented by a deflection of 1 cm. in 25 seconds was obtained. But when the light and slit were adjusted as in Fig. 3 and the same potential was applied the deflection was practically the same, namely 1 cm. in 23 sec. Again when

[1] PHYS. REV., Vol. 1, No. 3, March, 1913.

[2] Photo Electricity—Hughes, p. 25.

the apparatus was adjusted as in Fig. 4 the same deflection was obtained, namely 1 cm. in 24 sec. Practically the same currents were obtained in

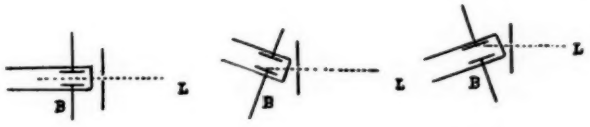

Fig. 2. Fig. 3. Fig. 4.

the three positions when 396 volts were applied, namely 5 cm. in 5 sec. At a conservative estimate 50 times as much light fell on the electrode in Figs. 3 and 4 as in Fig. 2.

The fact that the currents were the same regardless of the quantity of light that fell upon either electrode would seem to show that the effect observed could not be due to photo-electric action at either electrode. The photo-electric current from a metallic surface is proportional to the intensity of the light falling upon the surface. The presumption is thus raised that the effect observed is due to the vapor and the electrodes are not photo-electric for ordinary light.

A second test was made as follows: The bulb containing the potassium was kept at room temperature and the portion of the tube containing the electrodes was heated. The result would naturally be to drive vapor out of the main tube into the bulb. As the rate of diffusion in a tube of this type and at the temperature used is probably very slow, the temperature was raised to 65° Centigrade and kept there for several hours. The photo-electric currents were measured at various intervals. The result was that the photo-electric action at first increased and then gradually decreased. Neither the tube nor the light were touched nor altered in any way during this test so conditions were identical throughout except for the change in temperature and the lapse of time. The effect of mere lapse of time was tested and found not to influence the activity of the tube materially. It was found, however, that applying an E.M.F. and light for any considerable time did reduce the activity. Consequently complete ionization curves were not attempted but two different E.M.F.s, both positive and negative, were applied and the light was allowed to shine between the electrodes only for a very brief time during each test. No perceptible fatigue could result from that amount of use.

The curves *I* and *II*, taken for + 280 volts and + 287 volts, and curves *III* and *IV*, for − 280 and − 287 volts, show an increase and then a gradual decrease in the photo-electric currents. The ordinates represent the rate of deflection or the current. The abscissae represent the irregular intervals of time between tests. The temperature of the tube except at the

beginning and during the last interval of time was kept at about 65 degrees. At the beginning and throughout the 16-hour interval at the end of each curve the temperature was about 20 degrees.

These curves seem to show that the effect observed is a vapor effect. When the temperature is first raised the small amount of potassium which has collected in the main part of the tube begins to vaporize and the photo-electric action increases. When all the potassium in the main tube has been vaporized the density of the vapor there is reduced on account vapor being driven into the cold bulb. As the density of the vapor lessens the photo-electric action diminishes.

The effect of changing the pressure without changing the temperature in the main tube was next tried. It was believed that an electrode effect would show an increase of current when the pressure decreased while a vapor effect would show a decrease with decrease of pressure. The bulb was packed in salt and ice and kept at an average temperature of $-8°$ Centigrade for three hours. Brief ionization curves were taken just before and at the close of this period. Curves *V* and *VII* were obtained before reducing the pressure and curves *VI* and *VIII* after. As the photo-electric effect was plainly reduced it seems that the effect was due to the vapor.

The reason that much lower voltages were re uired in this last test than in the previous tests was that the whole tube including the bulb had been strongly heated for several hours. This greatly increased the quantity of vapor between the electrodes.

Surface effects were sometimes met with in making these tests. After the tube had been strongly heated and a narrow beam of light passed between the electrodes the electrometer showed a negative deflection with no E.M.F. applied. The beam of light struck the end of the tube as indicated by the dotted lines in Fig. 5. When the beam was adjusted to shine between the electrodes without touching the upper or lower wall of the tube as in Fig. 6 the effect disappeared. It was due to electrons released from solid potassium at the top or bottom of the tube.

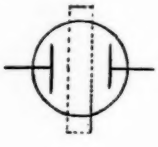

Fig. 5.

Fig. 6.

The fact that it is possible to obtain a regular ionization curve for positive as well as negative E.M.F.s is additional evidence that the effect is a vapor effect.

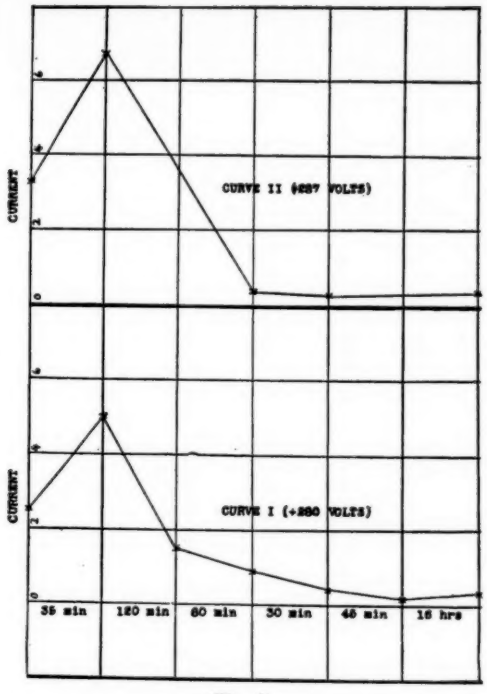
CURRENT
CURVE II (+287 VOLTS)
CURRENT
CURVE I (+280 VOLTS)
35 min
120 min
60 min
30 min
45 min
18 hrs

Fig. 7.

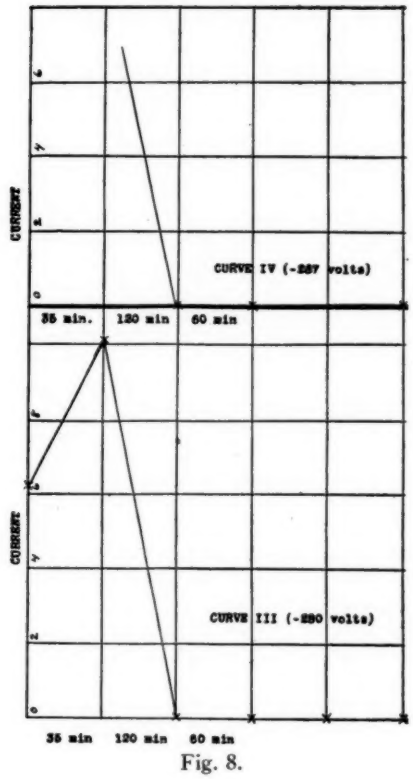
CURRENT
CURVE IV (-287 volts)
35 min.
120 min
60 min
CURRENT
CURVE III (-280 volts)
35 min
120 min
60 min

Fig. 8.

In conclusion there are four lines of reasoning which seem to show that potassium vapor is ionized by ordinary light.

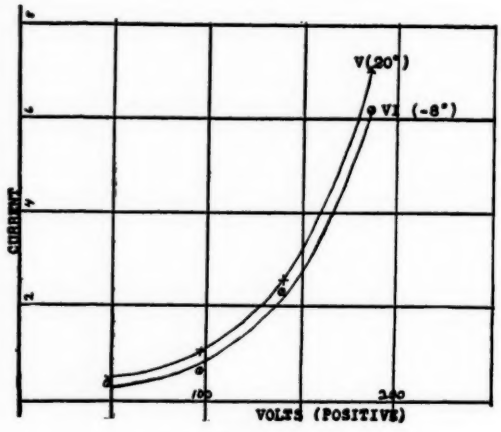

Fig. 9.

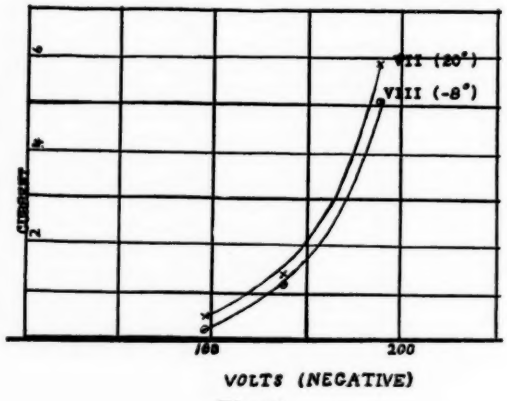

Fig. 10.

1. When a beam of visible light is directed first on one electrode then on the other, then midway between the electrodes the photo-electric currents are very nearly the same.

2. When the temperature of the main part of the tube is raised and the vapor driven into the cold bulb the photo-electric currents decrease.

3. When the temperature of the bulb is lowered thereby decreasing the pressure of the vapor throughout the tube, the photo-electric currents decrease.

4. The fact that ionization currents of approximately the same magnitude are obtained with both positive and negative E.M.F.s applied, is an indication that we have here an ionization of the vapor.

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THEORY OF VARIABLE DYNAMICAL-ELECTRICAL SYSTEMS.

BY H. W. NICHOLS.

COMPARED with the volume of literature on the subject of electrical and mechanical systems with invariable elements—resistance, inertia or inductance, stiffness or capacity—very little has been published concerning systems in which these elements are variable in a general way, and this notwithstanding the fact that such important applications as electric signaling depend upon the variability of some element of the system. The problem is usually to find the effect upon a steady or quasi-steady state of changes in some element, and the steady state is often not of interest, so that its existence is ignored. The ignoring of the undisturbed state but not of the energy which is transformed from it by the variable elements leads to many interesting and important problems, some of which are considered in this paper.

A more formal statement of the problem to be solved is: A dynamical-electrical system capable of description by means of differential equations obtained from a Lagrangian and a Dissipation function of the usual type is operating under the influence of given impressed forces. This state of the system is disturbed by changes in an inertia, resistance or stiffness element and the disturbed state is considered by itself, the undisturbed state being ignored if its motions are of types (defined later) different from those of the disturbed state.

It will be found that energy can in this way be added to the disturbed state in a manner similar to that in which it is " lost " from a dynamical system by transformation to a type with which the purely dynamical problem is not concerned, namely the energy of thermal agitation of systems whose coördinates are not required to be included in the Lagrangian function in order to obtain a satisfactory solution of the larger scale dynamical problem.

A very simple illustration of a system of this kind is an electric bell or " buzzer." From one very practical point of view the dynamical system of interest comprises only the button with its impressed force and the vibrating armature, so that the type of motion obtained bears no relation to that of the source (for example, a battery) nor is there any necessary relation between the energy of the motion and the work done by the

impressed force at the button. From another point of view the system is a generator of oscillations, either electrical or mechanical, without energy supply at the frequency of the oscillations and deriving its energy from a source which may be ignored if only oscillatory states are of interest.

From the point of view here taken it is convenient to classify dynamical-electrical systems into the following types, the first two of which are the ones ordinarily considered and the last two are of particular interest because such systems are capable of bringing energy into play from sources of different kinds, as will be explained later.

Types of Systems.—1. All purely electrical systems (whose motions do not involve the changing of a mechanical coördinate) and those in which the variables are measured from equilibrium positions, the generalized displacements x being small, are characterized by Lagrangian and Dissipation functions which are homogeneous quadratic functions of the displacements and velocities and have constant coefficients. As a result the system of differential equations of motion is a set of linear equations of the form:

$$\begin{aligned} S_{11}x_1 - S_{12}x_2 - S_{13}x_3 &= e_1 \\ -S_{21}x_1 + S_{22}x_2 - S_{23}x_3 &= e_2 \\ \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \end{aligned}$$

Here any stiffness operator S has the form

$$S = lp^2 + rp + s; \quad p = d/dt$$

and e is a given function of the time, being an impressed force. This system is characterized by the fact that its operational determinant $|S_{11}S_{nn}|$ is symmetrical, since the Lagrangian and Dissipation functions are of the specified type, and by the fact that it satisfies the energy principle. Due to these facts, the reciprocal theorem holds, namely, if C_{jk} represents the operator which finds the displacement x_j from unit driving force at the place k, or the mutual compliance between j and k:

$$C_{jk} = \frac{D_{jk}}{D}$$

where D is the operational determinant of the system and D_{jk} the minor of row j and column k. But when a unit driving force is located at j it produces at k the symbolic displacement $C_{kj} = D_{kj}/D$; and because D is symmetrical, $D_{jk} = D_{kj}$. Hence the two mutual compliances are the same. Such a system has been called bilateral.

The set of linear equations above has the further property that, if the driving forces are periodic and are resolved into their Fourier com-

ponents, all these components will in general appear in the particular solution for any x, and no others will ever appear. This is because the coefficients are constant, and this property will be described by saying that the system cannot change the *type* of driving force. This feature is important in many applications.

2. When the coördinates of interest are the small departures from zero values in a state of motion, the Lagrangian function is not a homogeneous quadratic one but leads to a set of differential equations of the form:[1]

$$S_{11}x_1 - (B_{12} + C_{12})x_2 - (B_{13} + C_{13})x_3 - \cdots = e_1$$
$$-(B_{21} - C_{21})x_1 + S_{22}x_2 - (B_{23} - C_{23})x_3 - \cdots = e_2,$$
$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

in which C_{jk} has the form $R_{jk}p = R_{kj}p$.

If the kth equation is multiplied by px_k and the results added, the terms in C cancel and hence do not enter into the equation of activity. Systems of this kind are different from those of the first class in that the reciprocal theorem does not hold. They resemble them, however, in reproducing the type of driving force. While the C's are of odd order in p, they do not contribute odd order terms to D, although they do to its minors. These centrifugal terms correspond formally to mutual resistances, but differ from ordinary dissipative terms in that they occur in pairs in such a way as to make the determinant D of even order in p so long as true resistances are not present. This is suggestive, as it indicates the possibility of compensating true resistances by similar terms, and the general conditions under which this may be accomplished will be discussed later. It is evident that in order to do this there must be a transformation of energy from that of an ignored type of driving force, otherwise an uncompensated flow of energy takes place out from the system through the resistances.

Energy dissipated as heat is of course not lost, but simply transformed into a type which is ignored in purely dynamical-electrical problems as outside the scope of the investigation. In the same way energy may be thought of as entering the system from an ignored source through suitable devices for changing its type into one with which the problem is concerned. The principal object of this paper is to investigate systems in which this occurs.

3. When the differential equations of the system are linear but with coefficients which are functions of the time, the system is characterized by the very important fact that it is able to execute motions whose types are different from those of the driving force, that is, the particular solu-

[1] See, for example, Whittaker, Analytical Dynamics, p. 84.

tions no longer correspond in component frequencies to the driving forces. If therefore some driving forces are of types which are ignored for the purposes of the investigation, perhaps because they have no direct influence upon certain parts of the system, it is possible to supply energy to the system in a way similar to that in which it is drawn off as heat. The definition chosen for the *type* of driving force or motion is now shown to be a suitable one, for when no energy is transformed to ignored types of any kind, the particular solutions depend upon the then pure imaginary roots of $D = 0$.

4. When the differential equations of the system are non-linear, the principle of superposition no longer holds, which fact is of considerable importance in some applications. Non-linearity often means that all the mechanism of the system has not been taken into account.

I. SYSTEMS WITH INVARIABLE ELEMENTS.

The classification adopted is a convenient one for our purposes and will be followed in this treatment, beginning with the first two classes. These are the cases ordinarily considered, and will be taken up only very briefly to collect some useful results, all of which, however, are no doubt old.

The coefficients of p^n in the differential equations:

$$\begin{aligned} S_{11}x_1 - S_{12}x_2 - \cdots &= e_1 \\ -S_{21}x_1 + S_{22}x_2 - \cdots &= e_2 \\ \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot & \end{aligned}$$

being constants, p may be treated as an algebraic quantity, with the result that any x has the value

$$x_k = \frac{\Sigma D_{jk} e_j}{D}.$$

If e_j is the only driving force acting,

$$x_k = \frac{D_{jk} e_j}{D}$$

and the operator D_{jk}/D is called the mutual compliance, C_{jk}, between the parts k and j, being the operator which finds the displacement produced at k by a driving force at j. The use of such operators apparently originated with Heaviside. For systems of the first class, $C_{kj} = C_{jk}$. When $k = j$ the compliance is self instead of mutual.

In certain special cases in which the driving forces are special functions of the time, these operators reduce to algebraic quantities. Some of the important results are considered below.

Steady State.—If in C_{jk}, the operator p is put equal to zero, the solution obtained is that appropriate to the final steady state under the influence of a constant driving force.

Harmonic State.—When p is put equal to $in + \delta$, the solution is that appropriate to an exponentially increasing or decreasing harmonic driving force of frequency $n/2\pi$ and damping δ, and in the extremely important case in which $\delta = 0$, the solution is that for an undamped harmonic driving force of frequency $n/2\pi$. The highly developed subject of alternating currents and of sustained simply periodic motions in general, depends largely for its practical value upon this method of reducing the differential equations to algebraic ones.[1]

When the driving force is harmonic, putting $p = in$ reduces any x to the quotient of two determinants whose elements are complex numbers. Further, since any S_{qs} enters linearly into the determinant D, any x_k must be of the form (omitting all subscripts for brevity):

$$x = \frac{aS + b}{cS + d},$$

or a bilinear transformation of S. This is the reason alternating current loci are circles.

When this transformation is thrown into its three constant form by division by c (which obviously cannot be zero for any physical system) it becomes:

$$x = \frac{a}{c} - \frac{1}{c^2}\frac{ad - bc}{S + d/c} = J - \frac{\Delta}{S + K},$$

the constants of which should and do have physical significance, namely:

When $\Delta = 0$ a change in S has no effect upon x; these two parts of the system are conjugate. Hence to have conjugate parts a system, if connected at all, must have at least three degrees of freedom.

J is the value of x when S is infinite, that is, when the branch having the operator S is removed.

When K is zero or Δ/J reduction of S to zero produces infinite and zero values, respectively, of x.

Many other relations may be found involving this transformation. It is useful in experimental work, being established by three points.

In practical work, for example in alternating currents, it is usual to ignore the operational nature of these quantities S, etc., and treat them in the same way as the forces, displacements and velocities themselves; that is, complex numbers, $a + ib$, are used for both operators (O) and

[1] For a concise and valuable treatment of this case ($p = in + \delta$) see G. A. Campbell, Proc. A. I. E. E., April, 1911.

physical quantities (T), the latter being functions of the time, which variable is eliminated in single frequency problems by this method. Consequently no distinction is made between products such as OT and TT, which are physically very different things, the first being of frequency $n/2\pi$ and the second having a constant part and a part of double frequency, n/π, that is, not being capable of representation in the complex plane of T. Thus if

$$O = a + ib, \quad T = c + id,$$

the formal product OT gives a physically intelligible result, while the formal product $TT = c_1c_2 - d_1d_2 + i(c_1d_2 + c_2d_1)$ has no physical significance. In particular, it does not represent power, torque, etc. Steinmetz avoided this difficulty by giving up the rule $i \times 1 = 1 \times i$ for these products, but it seems better[1] to introduce a double frequency operator, say k, represented geometrically by a unit vector at right angles to 1 and i, such that

$$O = a + ib + ko,$$

$$T = c + id + ko,$$

as before, to retain the formal operations OT, but to define the complete product TT of two physical quantities as the sum of the scalar and vector products:

$$T \cdot T + T \times T = c_1c_2 + d_1d_2 + k\begin{vmatrix} c_1 & c_2 \\ d_1 & d_2 \end{vmatrix} = P + kQ.$$

This gives the correct value (in contrast to formal multiplication) and moreover indicates, by the unit operators 1 and k, the nature of the result with respect to frequency. In problems in which both time differentiations and multiplications TT are required, there is some advantage in using this method and it will be used here when necessary.

Impulses and Initial Values.—When p is made infinite in the compliance operator, the initial values of the coördinates are found.

When a driving force e_j is impulsive, its impulse being

$$I_j = \operatorname*{Lim}_{\substack{t=0 \\ e_j=\infty}} \int^t e_j dt,$$

we have $e_j = pI_j$, which may be substituted in the differential equations to find the behavior under this kind of excitation. An advantage of this method of treatment is that the initial conditions may be found from the differential equations; thus the initial displacements are

$$x_k(o) = \operatorname*{Lim}_{p=\infty} (pC_{jk}I_j),$$

[1] Armour Engineer, January, 1912.

and the initial velocities

$$\dot{x}_k(o) = \operatorname*{Lim}_{p=\infty}(p^2 C_{jk} I_j).$$

In general, since $C_{jk} = D_{jk}/D$ and the order of D is two higher than that of D_{jk}, the initial displacements are zero, the initial velocities finite, and the initial accelerations infinite for impulsive excitation. This ceases to be the case when inertia terms are lacking from some of the elements, when some initial velocities may be infinite. $(pC_{jk})^{-1}$ and $(p^2C_{jk})^{-1}$, with p infinite, are respectively the initial resistance and initial inertia offered at the place k to a sudden disturbance acting at the place j.

Free Oscillation.—The condition of free oscillation of the system is that $D = 0$, which equation gives the values of $p = in + \delta$ corresponding to the frequencies and damping constants of the component oscillations. If the free oscillations are *sustained*, $\delta = 0$.

Since the condition $D = 0$ is also the condition that the effect produced by a given driving force shall be the largest possible, it is clear that the two requirements of good signaling, namely that the effect x shall be both a large and a true copy of the cause e for all wave forms, are in general contradictory; for the condition that x shall be largest is also the one that the system shall oscillate without regard to the driving force. In this case the " quality " of reproduction is zero. (It is highly desirable to develop some dynamical specification of quality of reproduction which corresponds to and predicts data furnished by the senses.)

There are two obvious exceptions to this statement, one the case in which the compliance C is of one kind and also independent of p, the other the case of an infinite number of degrees of freedom, to which this argument does not necessarily apply.

II. Systems Having Variable Elements.

When the inertia, resistance, or stiffness factors are variable with the time only, the differential equations of the system are linear with variable coefficients and the importance of this class of systems depends, from our point of view, upon the fact that the particular solutions contain types of motion different from those of the driving force. The variation which is most important is that in which the magnitude never departs greatly from a mean value and in cases of physical interest it is then possible to find a solution in the form of a convergent series as has been done, for example, by Barkhausen,[1] Pupin and others, using a method of successive approximation. The object of this paper, however, is not primarily to find the coefficients in such an expansion, but to show

[1] "Problem der Schwingungserzeugung," 1907.

how the transformation of energy from one type to another leads to useful results.

Considering any generalized stiffness factor with constant elements,

$$S = lp^2 + rp + s,$$

it is clear that when l, r, and s are variable S must be written

$$p(lp) + rp + s = lp^2 + [r + (pl)]p + s,$$

so that if

$$l = l_0 + \lambda, \quad r = r_0 + \rho, \quad s = s_0 + \sigma,$$

the change in S is

$$\Delta S = \lambda p^2 + (\rho + \lambda')p + \sigma.$$

This interpretation of ΔS will be understood in what follows.

In the set of linear equations

$$\begin{aligned} S_{11}x_1 - S_{12}x_2 - \cdots &= e_1 \\ - S_{21}x_1 + S_{22}x_2 - \cdots &= e_2 \\ \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot & \end{aligned}$$

let S_{11} be the variable element. This can always be done, if necessary, by a linear change of variable. Put $S_{11} = S_0 - \delta S$ and call D_0 the value of D when $\delta S = 0$. Also let

$$x_k = X_k + \xi_k$$

in which

$$X_k = \frac{\Sigma D_{jk} e_j}{D_0}.$$

If these values are substituted in the set of equations above we get

$$\begin{aligned} (S_0 - \partial S)\xi_1 - S_{12}\xi_2 - \cdots &= \delta S X_1 \\ - S_{21}\xi_1 + S_{22}\xi_2 - \cdots &= 0 \\ - S_{31}\xi_1 - S_{32}\xi_2 + \cdots &= 0 \\ \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot & \end{aligned} \tag{A}$$

and any ξ is therefore:

$$\xi_k = \frac{D_{k1}}{D}\delta S X_1 = \frac{D_{k1}}{D_0}\left(1 - \delta S \frac{D_{11}}{D_0}\right)^{-1} \delta S X_1$$

$$= \left\{ 1 + \delta S \frac{D_{11}}{D_0} - \left(\delta S \frac{D_{11}}{D_0}\right)^2 + \cdots \right\} \frac{D_{k1}}{D_0} \delta S X_1. \tag{1}$$

This equation shows that, so far as first order terms in δS are concerned, the disturbance superposed upon the unvaried system may be accounted for by supposing the sources of the unvaried motion removed and replaced by a driving force equal to $\delta S X_1$ whose seat is in the variable

element, the constants of the system remaining the same. It shows also that, with a proper interpretation of the symbols, the driving force for large or small values of δS is

$$\Xi = \frac{\delta S x_1}{1 - \delta S \dfrac{D_{11}}{D_0}},$$

since when this is operated upon by D_{k1}/D_0 the result is ξ_k.

There is, however, one very important difference between this system and one without ignored sources and excited by the same driving force, for in the latter case all the power expended in the system comes from the driving force, while in the former case the power may come from impressed forces required to produce the variation δS (that is, from the equivalent driving force) or it may come from the sources maintaining the ignored state, in which case the variable element acts as a transformer of energy from one type to another. These two rôles are essentially different ones and will be discussed in detail shortly, after a few consequences of equation (1) are noted.

It follows from that equation that if ξ is intended to be a copy of the variation δS, the copy cannot be perfect unless $D_{11} = 0$, which means that the compliance of the system, measured from the variable branch, shall be zero. Consequently a perfect copy of the variation of a stiffness factor S cannot be obtained with finite displacements. The terms of degree higher than the first in δS indicate distortion, or departure from perfection of the copy otherwise than through resonant selectivity of the system. An illustration is a microphone telephone transmitter, in which the electrical copy of the motion of the diaphragm is desired to be perfect.

It is evident that forces f_j, of non-ignored type, may be added to the system in the usual way, and the right hand members of (A) will be supposed increased by these impressed forces of ξ-type.

To evaluate ξ in algebraic terms, $\delta S X_1$ must be reduced to a function of time, say $\phi(t)$, and $\delta S D_{11}/D_0$ to the form $F(t) \cdot P(p)$; then the solution is the sum of terms such as

$$\xi' = \frac{D_{11}}{D}\phi(t), \quad \xi'' = F(t) \cdot P(p)\xi', \quad \xi''' = -F(t)P(p)\xi'',$$

etc.

A few simple examples will be given to show the application.

(*a*) Consider an electrical circuit containing inductance l, resistance r, capacity $1/s$ and a constant source of E.M.F. E. The elements are in series. Let the stiffness of the condenser vary as $s_0(1 - a \cos nt)$. The steady state is $X_1 = E/s_0$ and

$$\xi = \left(1 + \frac{a\cos nt}{S_0} - \cdots\right)\frac{aE\cos nt}{S_0},$$

where

$$S_0 = lp^2 + rp + s_0.$$

Since $1/S_0$ operating upon any periodic function can always be evaluated, the expansion can be carried out.

(*b*) If the battery is replaced by an alternator of voltage $E\cos qt$, we get

$$X_1 = \frac{Ee^{iqt}}{S_0(iq)}; \quad \delta SX_1 = A\cos[(q+n)t+\alpha] + B\cos[(q-n)t+\beta].$$

Hence ξ contains terms of frequencies proportional to $q \pm n$, and higher order terms of frequencies proportional to $q \pm kn$, $k = 1, 2, \cdots$.

(*c*) If, in this circuit, the resistance is varied according to $r(1-a\cos nt)$, we have $\delta SX_1 = ar\cos nt \cdot pX_1$ and no disturbance is produced unless X_1 is a function of the time, that is, unless the E.M.F. E is variable. If, however, the condenser is shunted by an infinite perfect inductance we have, for a constant E.M.F.

$$X_1 = E/rp; \quad \delta SX_1 = aE\cos nt.$$

(*d*) If, in the last circuit, the inductance is variable so that

$$\delta S = al\cos nt \cdot p - anl\sin nt \cdot p$$

with $X_1 = E/rp$ we get

$$\delta SX_1 = -aEnl/r \cdot \sin nt,$$

and the part $al\cos nt \cdot p$ of the stiffness δS has no influence because the current pX_1 is constant. Finally, if the circuit carries an alternating current

$$pX_1 = A\cos qt,$$

we find

$$\delta SX_1 = B[(q+n)\sin(q+n)t + (q-n)\sin(q-n)t].$$

So far no account has been taken of the manner in which the variation δS is produced, while if a complete description of the behavior of the system is to be had, the dynamics of the variable element must be included in the system of equations. If the energy represented by the ξ-system comes from forces required to produce the variation δS, the principle of energy will be satisfied by including these forces and no liberation of energy from the original state will take place. If, on the other hand, the energy of the ξ-system comes from the ignored state and is simply set free by the action of forces producing the variation, the principle of energy will not be satisfied for that system and there will be no particular relation between the energy of the latter forces and the

energy set free by them. This is a very important distinction; for example, in the problem of the telephone amplifier and of generators of sustained oscillations the energy which is transformed must come from an auxiliary and ignored source.

To determine the source of the energy of the disturbed state, consider how variations in any element are produced. Any inertia, resistance or stiffness factor, or in the electrical case, any inductance, resistance or capacity, is fixed by geometrical coördinates and by quantities of the nature of permeability, dielectric constant, etc., depending upon the properties of materials. The geometrical coördinates and electrical charges are the variables chosen to represent the state of the system, together with these material constants whose dynamical natures are either not known or supposed not known. With these the Lagrangian and Dissipation functions are built up, the equations of motion being then found from

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{x}} - \frac{\partial L}{\partial x} + \frac{\partial F}{\partial \dot{x}} = E.$$

Now L is a function of the coördinates x and their velocities $\dot{x}$ and is differentiated by each to find the reactions; hence any change in the geometrical shape of any system of electrical conductors or other bodies, and the forces thereby brought into play, are included in the dynamics of the system. It therefore follows that any energy derived from the change of geometrical form of any inductance, capacity, inertia or stiffness of the system comes from impressed forces tending to change this geometrical form and is taken account of in the equation of energy. In particular, in any complete cycle of operations, no energy comes from the undisturbed state of the system, hence *no energy of an ignored type is continuously transformed by the variation of the geometrical coördinates determining any inductance, capacity, inertia or stiffness factor of the system.*

On the other hand, forces due to the variation of material constants in the Lagrangian function L are not included in the dynamical equations obtained by Lagrange's method and hence the energy set free or transformed by their variations may come from that of the undisturbed state.

An example of this is found in the case of a deformable inductance coil. If the coil is energized by a battery and then deformed so as to vary periodically the inductance of the circuit and thus produce an alternating current in it, all the power represented by that alternating current will be derived from mechanical forces required to vary the shape of the circuit. Such a device could not be used to bring into play an auxiliary source of energy of different type—for example, it could not be made into a telephone amplifier. An ordinary telephone receiver is also a system of this kind.

The same thing is true in the case of a condenser whose geometrical dimensions only are varied, for here the forces resisting deformation are derived from the Lagrangian function and enter into the activity equation.

If in the coil the permeability of the medium is varied without mechanical motion of it as a whole, and hence the inductance varied without varying any geometrical coördinate entering into the Lagrangian function, the energy of the varied state must be derived from the battery. It may require energy to produce the variation in permeability, but the amount of this energy may be quite different from that transformed from the auxiliary source and will depend upon different things. The same remarks apply to the variation of the dielectric constant of a condenser without bodily motion of the medium itself.

The Dissipation function F is also a function of the coördinates and their velocities, together with constants of materials, but in the equations of motion only its partial derivatives with respect to the velocities appear. Hence if *either* the geometrical dimensions of resistances or the specific resistance constants of materials vary with the time, the impressed forces required are not part of the dynamical scheme described by the Lagrangian equations. The energy of the disturbed state must come from the sources of the undisturbed state, while the energy required to vary the resistances need have no necessary relation to that brought into the system from the ignored sources. Any resistance variation, however produced, is able to transform energy from the undisturbed state to the disturbed one.

From this discussion it follows that the only variations not already taken account of in the ordinary equations of motion are those in which a permeability, density, dielectric constant, elastic constant, or a resistance is changed. These are therefore the ways in which energy can be transformed from the sources of the undisturbed state, and in what immediately follows the variation δS of the stiffness will be supposed to contain explicitly only these parts, any other part being already included in the equations of motion as obtained by Lagrange's method. These variations, as well as the resulting motions, will first be supposed small in order that the equations may remain linear.

To take account of the variations produced in the way just discussed, we will now suppose that δS depends upon some mechanical or electrical coördinates $x_1 \cdots x_N$, $x_{N+1} \cdots x_{N+M}$ and consequently upon $\xi_1 \cdots \xi_{N+M}$ in a way described by the differential equation

$$\delta S = \sum_{j=1}^{N+M} \phi_{1j}(p)\xi_j,$$

which is apparently sufficiently general to include all cases in which the equations remain linear.

The variation δS may depend upon M coördinates not required for the specification of the original system which is not concerned with the mechanism producing this variation, as well as upon the N coördinates originally required. (We might also suppose that a number of elements were varied, with

$$\delta S_k = \sum_1^{N+M} \phi_{jk}(p)\xi_j; \quad k = 1 \cdots N,$$

but it follows from the previous discussion that no generality is added thereby.)

The system $(\xi_{N+1} \cdots \xi_{N+M})$, which represents the additional mechanism by which δS is determined, will be supposed subject to laws capable of statement by linear differential equations, and the driving force $\delta S X_1$ will be written

$$\Sigma \phi_{1j}\xi_j X_1 = \Sigma Q_{1j}\xi_j.$$

The differential equations of the system, including impressed forces of ξ-type, will now be of the form:

$$\begin{array}{l|l}
(S_{11} - Q_{11})\xi_1 - (S_{12} + Q_{12})\xi_2 \cdots - (S_{1N} + Q_{1N})\xi_N & -Q_{1,N+1}\xi_{N+1} \cdots = f_1 \\
-S_{21}\xi_1 + S_{22}\xi_2 \cdots - S_{2,N}\xi_N & 0 \cdots = f_2 \\
\hline
0 \quad 0 \quad \cdots \quad 0 & S_{\substack{N+1 \\ N+1}}\xi_{N+1} \cdots = f_{N+1} \\
\cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot & \cdot \quad \cdot \quad \cdot \quad \cdot \\
0 \quad 0 \quad \cdots \quad 0 & \cdots \quad S_{\substack{N+M \\ N+M}}\xi_{N+M} = f_{N+M}
\end{array}$$

Aside from the fact of the variability of S_{11} (which variation may be supposed to be small) this system differs from those discussed in part I in that *there is no necessary relation* between $S_{1k} + Q_{1k}$ and S_{k1}. Consequently *the equation of activity is not satisfied for the ξ-system, but energy is continuously drawn into the system from the ignored sources through the periodically variable element.* The energy so drawn is, per unit time:

$$P = \frac{1}{T}\Sigma \int_0^T Q_{1j}\xi_j \dot{\xi}_j dt.$$

We have now succeeded in making S_{kj} different from S_{jk} in a way not accounted for by centrifugal terms and such that $S_{jk} - S_{kj}$ may have practically any form, depending upon the dynamical nature of the mechanism by which S is varied. This system obviously need have no special relation to the original one; in fact, if no impressed forces act upon the additional coördinates $\xi_{N+1} \cdots \xi_{N+M}$ required to completely determine δS, that system has no effect upon the solution for any original coördinates except through the Q-terms, for if

$$D^{(N)} = |S_{11}S_{NN}|$$

any original coördinate is

$$\xi_k = \frac{\sum_1^N {}_1D_{jk}{}^{(N)} f_j}{D^{(N)}}, \quad k = 1 \cdots N,$$

and contains no explicit reference to the additional mechanism producing the variation δS.

Since we are treating the original system $\xi_1 \cdots \xi_N$ as the one whose dynamical nature is known, or as the only one upon which measurements are to be made, it is appropriate to eliminate the coördinates $\xi_{N+1} \cdots \xi_{N+M}$ from explicit appearance; moreover this is suggested by the form of the determinant above. For these reasons imagine the last M equations to be solved for the coördinates appearing in them. Let the result of this be substituted in the first N equations and put $Q_{N+i}\xi_{N+i} = g_{1i}$, the g's being expressed in this way in terms of the impressed forces $f_{N+1} \cdots f_{N+M}$. We then get for the equations of motion

$$\text{(B)} \quad \begin{cases} (S_{11} - Q_{11})\xi_1 - (S_{12} + Q_{12})\xi_2 \cdots - (S_{1N} + Q_{1N})\xi_N = f_1 + \Sigma g_{1j} = f_1 + g_1 \\ \quad - S_{21}\xi_1 \quad + S_{22}\xi_2 \qquad \cdots \qquad\qquad\qquad = f_2 \\ \quad \cdot \quad\quad \cdot \quad\quad \cdot \quad\quad \cdot \quad\quad \cdot \quad\quad \cdot \quad\quad \cdot \quad\quad \cdot \quad\quad \cdot \\ \quad - S_{N1}\xi_1 \qquad \cdots \qquad\qquad \cdots \quad + S_{NN}\xi_N \qquad = f_N. \end{cases}$$

which contain explicitly only the original variables, and from which the following fundamental theorem is obtained:

The effect of the ignored sources and of the mechanism by which the small variation δS is produced is to make the original system appear from dynamical-electrical measurements on the ξ-variables only as one in which S_{11} is changed to $S_{11} - Q_{11}$, any S_{1k} to $S_{1k} + Q_{1k}$, and the impressed force f_1 to $f_1 + g_1$.

These equations are the fundamental ones in the study of systems to which energy is added by transformation from ignored sources, and to make clear the meaning of the terms a few special cases will now be considered. First supposed that no impressed forces act upon the coördinates $\xi_{N+1} \cdots \xi_{N+M}$ so that $g_1 = 0$ ultimately. Also suppose all the Q's are zero except Q_{11} which will be written $ap^2 + bp + c$. The equations then show that the system behaves as one in which the stiffness S_{11} is $(l_{11} - a)p^2 + (r_{11} - b)p + (s_{11} - c)$ so that the inertia, resistance and stiffness, or the inductance, resistance and (capacity)$^{-1}$ have been decreased by the (positive or negative) amounts a, b, c, respectively. The quantity $-b$ is called a "negative resistance" for obvious reasons. The power added to the system by means of it, or the negative power

dissipated by it, is $b\xi_1^2$, hence proportional to the square of the velocity ξ_1 as is the heat produced in the resistance r_{11}. Energy is thus brought into the system by the same general type of ignored mechanism as that by which it passes out of the purely dynamical or electrical system.

The effects of a and c are changes in the storage of power and hence in the resonant frequencies and phases of forced oscillations. An ordinary electric bell is a simple example of this kind of system, especially if the contact is shunted with a resistance of a few ohms so that the resistance changes are not too large.

Second, if every Q is zero, but g_1 is different from zero we have the simplest case, namely, energy added through the trigger or relay action of impressed forces which vary only the eliminated coördinates and do not act upon the original system. A variable resistance telephone transmitter and an electric switch are illustrations. The power added is $g_1\dot{\xi}_1$.

Third, if every Q is zero except one with unlike subscripts say Q_{12}, and if $g_1 = 0$, the most noteworthy effect is that the determinant of the coefficients is neither symmetrical nor has it only the special skew-symmetric elements appropriate to centrifugal forces. The reciprocal theorem does not hold and we get, for example, putting Δ for the value of D when $Q_{12} = 0$:

$$\frac{C_{21}}{C_{12}} = \frac{\Delta_{21} - Q_{12}M_2}{\Delta_{12}}$$

where M_2 is a second minor of Δ. The mutual compliances may therefore be made widely different in two opposite directions through the system. Similar expressions obtain for other mutual compliances. Examples of systems having these characteristics will be worked out later in this paper.

Free Oscillations.—One of the most important cases is that in which all the impressed forces are zero. In this case no forces of ξ-type act upon the system and if it is to move and do work all the energy required must be transformed from the ignored sources. Such a system is called an oscillation generator.

If the coördinates are not to be zero the determinant D must vanish and its vanishing will determine values $p = p_1$, p_2, etc., which give the frequencies and damping constants of the oscillations. Now for the invariable systems occurring in pure dynamics it can be proved that the real parts of the roots of $D = 0$ are negative if there is any resistance in the system, so that *sustained* free oscillations of those systems cannot take place. This proof, however, does not apply to systems having the more general determinant here found, and we may expect sustained oscillations under proper conditions.

The condition of sustained free oscillation is that $D = 0$ with $p = in$. Suppose p is given this value in the equation $D = 0$ which will then become an equation in n with both real and imaginary coefficients. This equation is equivalent to two equations, say

$$F(n) = 0, \quad G(n) = 0,$$

which when solved simultaneously will give certain values of n and certain corresponding relations between the n's and the Q's. The latter relations are those which must exist in order that p shall be pure imaginary, or that the oscillations of frequency $n/2\pi$ shall be sustained. Hence in order to make the system perform certain free oscillations n, the transforming mechanism must be adjusted to give the corresponding values of the Q's, and by changing these values different oscillations will in general be possible. In this respect this kind of system differs from one merely devoid of resistances, which oscillates simultaneously in all possible modes except in special cases of normal coördinates, when special starting conditions are required.

The power dissipated in a system executing harmonic oscillations is

$$(S_{11}\xi_1 - S_{12}\xi_2 - \cdots) \cdot p\xi_1 + (- S_{21}\xi_1 + S_{22}\xi_2 - \cdots) \cdot p\xi_2 + \cdots$$

and the power transformed is

$$(Q_{11}\xi_1 - Q_{12}\xi_2 - \cdots) \cdot p\xi_1.$$

In the *sustained* free oscillations of the system these are equal, hence in that case the variable element transforms just enough power to supply the dissipation.

Since the effect of the variable element is to supply the dissipated power, it might be thought that to calculate the frequencies of sustained oscillation it would be necessary only to ignore all resistances, or better the dissipation in each branch by making the resistances zero or infinite. But the frequencies so obtained will not in general be the correct ones, even when the variable element introduces only negative resistances and does not change any reactance. As an example consider the case of a transformer:

$$D = \begin{vmatrix} L_1p^2 + R_1p + S_1 - bp & - Mp^2 \\ - Mp^2 & L_2p^2 + R_2p + S_2 \end{vmatrix} = 0.$$

We get, with all losses suppressed:

$$(L_1L_2 - M^2)p^4 + (S_2L_1 + S_1L_2)p^2 + S_1S_2 = 0,$$

while equating terms in odd and even powers of p separately to zero gives the additional term in the frequency equation:

$$R_2(R_1 - b)p^2.$$

The odd order terms are

$$p(R_1 - b)(K_2p^2 + S_2) + pR_2(L_1p^2 + S_1)$$

and these equations are inconsistent with $R_2(R_1 - b) = 0$ unless $M = 0$.

Moreover let $\pm p_1$ and $\pm p_2$ be the roots of the even part of $D = 0$ and substitute them in the equation for b. The result will be that in general $b(p_1)$ will be different from $b(p_2)$, so that the system, with a given value of b, will perform only a part of the possible oscillations.

Example.—A device which illustrates this theory and method is one for producing small alternating currents for laboratory use and known as the "microphone hummer." It consists of a bar B supported on knife edges above a magnet and carrying a carbon cell C through which flows current from a battery. Motion of the bar varies the resistance of the cell and consequently introduces an E.M.F. into its circuit which produces current in the magnet and sustains the oscillations under proper conditions. Sufficient energy is transformed from the battery to allow alternating current to be drawn off into a load resistance R. To solve this problem, take the case of the slightly more general arrangement shown in the next figure in which S_{12} represents any kind of coupling of the meshes 1 and 2 carrying the mesh currents $\dot{\xi}_1$ and $\dot{\xi}_2$. A' and A'' are infinite perfect inductances to restrict the direct currents to theirproper paths. Impressed forces are included as shown.

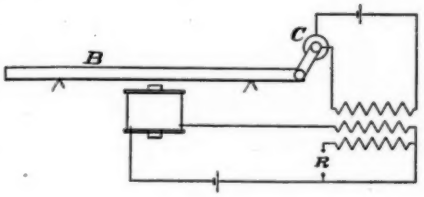

Fig. 1.

This system has a variable inductance in the magnetic circuit since the permeance of the magnetic circuit is a function of the displacement ξ_3. Since this variation is due to a change in the geometry of the figure it will be taken account of in the Lagrangian function as will be seen below. The inductance of the magnetic circuit is $L_0/(1 - a\xi_3)$ where L_0 is the average inductance, hence that part of the kinetic energy which depends upon the magnet is

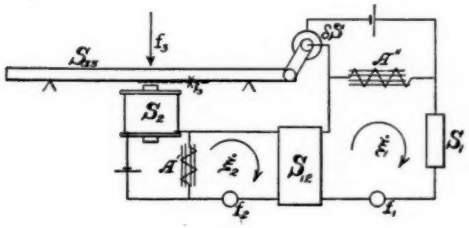

Fig. 2.

$$\tfrac{1}{2}L(I_2 + \dot{\xi}_2)^2 = \tfrac{1}{2}L_0(1 + a\xi_3)(I_2 + \dot{\xi}_2)^2,$$

where I_2 is the steady current through it. We therefore get, to first order terms:

$$\frac{\partial T}{\partial \xi_3} = aL_0 I_2 p\xi_2 + \text{constant} = \phi p\xi_2 + \text{constant}$$

$$\frac{d}{dt}\frac{\partial T}{\partial \dot{\xi}_2} = L_0 p^2 \xi_2 + \phi p \xi_3$$

and the equations of motion are therefore:

$$\begin{aligned} S_{11}\xi_1 - S_{12}\xi_2 \quad\quad\; 0 \quad\quad &= \partial SX_1 + f_1 = Q_{13}\xi_3 + f_1 \\ -S_{21}\xi_1 + S_{22}\xi_2 + \phi p\xi_3 \quad &= f_2, \\ 0 \quad -\phi p\xi_2 + S_{33}\xi_3 \quad &= f_3. \end{aligned}$$

Here δSX_1 is equal to the product of the direct current, I_1, through the microphone and its resistance change δr.

The determinant of the system is

$$D = \begin{vmatrix} S_{11} & -S_{12} & -Q_{13} \\ -S_{21} & S_{22} & \phi p \\ 0 & -\phi p & S_{33} \end{vmatrix}$$

It shows how the centrifugal terms ϕp appear due to the fact that the pull of the magnet is proportional to the square of the total current, and also how the symmetry fails when power is added through the term $Q_{13} = Q$.

Since the general theory is immediately applicable to the problem, only some very simple cases will be treated further. Suppose, for example, that the load is pure resistance, $S_1 = Rp$, and that the bar has effective mass m and stiffness s, its resistance being neglected. Also let the coupling $S_{12} = S_{21}$ be through a transformer of self inductances J, J, and mutual inductance M. The equations of the system now become:

$$\begin{vmatrix} Jp^2 + Rp & -Mp^2 & -Q & f_1 \\ -Mp^2 & Kp^2 & \phi p & f_2; \\ 0 & -\phi p & mp^2 + s & f_3 \end{vmatrix} \quad K = L + J.$$

Free Oscillations.—For this case, $D = 0$ with $p = in$, giving two equations with even and odd powers of p. Put $Q = A + Bp$ where A and B are even functions of p; then we get for $D = 0$:

$$\begin{aligned} G(mp^2 + s) + J\phi^2 &= M\phi B, \\ RK(mp^2 + s) + R\phi^2 &= M\phi A, \end{aligned} \qquad G = JK - M^2.$$

Here $A = a_0 + a_2 p^2 + \cdots, B = b_0 + b_2 p^2 + \cdots$.

These equations give a great deal of information; for example we may inquire what are the conditions under which the bar will oscillate in its own natural frequency, for which $-p^2 = s/m = n_0^2$. For this case $A = R\phi/M$, $B = J\phi/M$, and we get for the simplest dynamical connection between the resistance change and the coördinate ξ_3:

$$\delta SX_1 = \delta r I_1 = Q\xi_3 = (R\phi/M + pJ\phi/M)\xi_3.$$

Hence the resistance change must depend upon the displacement and the velocity according to the law

$$\delta r = \frac{J\phi}{MI_1}\frac{d\xi_3}{dt} + \frac{R\phi}{MI_1}\xi_3$$

in order that the oscillations shall be sustained and have the required frequency. In the instrument the microphone is mounted upon an arm which can be set at various angles to the axis of the bar and this allows the correct adjustment to be approximated. The resistance change probably depends upon the acceleration also, which, for this motion, is proportional to the displacement. It is easy to see that the power drawn into the system from the battery is equal to that dissipated in the load R.

We might also wish to know the frequency at which the system could oscillate for a given dynamical connection; as an example suppose the microphone is so fastened to the bar that the resistance change is proportional to the displacement. Then $A = a_0$, $B = 0$ and

$$-p^2 = n_0^2\left(1 + \frac{J\phi^2}{Gs}\right),$$

$$a_0 = \frac{R\phi}{M}\left(1 - \frac{JK}{G}\right).$$

The frequency is therefore increased and the current I_1 must be adjusted to give a_0 the proper value as set by the second equation. Note that if $\phi = 0$, that is, if the bar does not react upon the magnet, the frequency will be $n_0/2\pi$ and no power will be required from the battery to maintain the oscillation. If the damping of the bar is not assumed to be zero more interesting problems arise which may easily be worked out but are too long to be included here. In that case the damping of the bar has considerable influence upon the frequency (not the same as in the damped free oscillation of the bar *alone*) and this effect can be noticed in the instrument by damping the bar without adding to its inertia.

Forced Vibrations.—Imagine an alternator of frequency $n/2\pi$ acting in the mesh 1. The current in the load R will be

$$\dot{\xi}_1 = \frac{pD_{11}f}{D} = \frac{p\Delta_{11}f}{\Delta - Q\Delta_{13}},$$

where Δ is the value of D when $Q = 0$.

Now D/pD_{11} is the impedance offered by the system when measured from the terminals of the alternator, hence the effect of adding the transforming device is to change this impedance from

$$Z = \frac{\Delta}{p\Delta_{11}}$$

to

$$Z_Q = Z\left(1 - Q\frac{\Delta_{13}}{\Delta}\right).$$

The impedance may therefore be considerably decreased and also given very different reactance characteristics. This fact may be described by saying that the transforming device introduces into one of the terminals the *negative impedance* $-QZ(\Delta_{13}/\Delta)$. In fact, this is what would be indicated by measurements made with a Wheatstone bridge at those terminals.

If $Q(\Delta_{13}/\Delta) = 1$ we have $D = 0$ and the system offers no impedance at all. This is the case of free oscillations again.

Similar results obviously will be found if the alternator is connected into the other mesh or if a mechanical force acts upon the bar. The effect of the transforming mechanism is therefore to amplify the effect of an impressed force by supplying energy from a source of another type which has been ignored in the problem.

We may look at this problem in another way: thus suppose only electrical quantities can be measured so that the system is taken to be one of apparently but two degrees of freedom, both electrical, and information is to be gained only by operations upon them. Elimination of the mechanical coördinate by means of the last equation gives:

$$(Jp^2 + Rp)\xi_1 - \left(Mp^2 + \frac{Q\phi p}{mp^2 + s}\right)\xi_2 = f_1 + Qf_3/(mp^2 + s),$$

$$-Mp^2\xi_1 + \left(Kp^2 + \frac{\phi^2 p^2}{mp^2 + s}\right)\xi_2 = f_2 - \frac{\phi p f_3}{mp^2 + s}.$$

This system, especially in the neighborhood of $mp^2 + s = 0$, would act very differently from a purely electrical system. The two mutual compliances would be widely different (but still only if Q were not zero), the effect of the force f would be changed under the same circumstances, and for any finite coupling ϕ the effective stiffness factors would be changed.

Another Example.—A good illustration of free vibrations occurs in the case of the "howling telephone" which is formed by holding an electrically connected telephone transmitter and receiver together as shown in Fig. 3. the geometry of the system being there made as simple

as possible. The fact that the dynamical connection between the receiver diaphragm and the variable element is a column of air (assumed to move in one dimension only) adds interest to the problem.

Let the variable current be $\dot{\xi}_1$ and the displacement of the diaphragms ξ_2 and ξ_3. Then δr will be $h\xi_3$, say, and

$$I\delta r = Q\xi_2,$$

so that Q/hI expresses the dynamical connection between the two diaphragms.

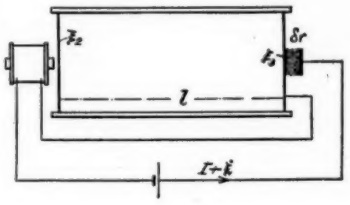

Fig. 3.

We may suppose h to be a number, although this is not necessary. The equations of motion are now similar to those of the last example, namely

$$(Lp^2 + Rp)\xi_1 - (Q - \phi p)\xi_2 = 0,$$
$$-\phi p\xi_1 + S_{22}\xi_2 = 0,$$

in which S_{22} means the stiffness offered by the diaphragm to an impressed force and consequently includes the loading due to the air column.

The condition of free vibration is

$$(Lp^2 + Rp)S_{22} = \phi p(Q - \phi p)$$

or for sustained oscillations

$$(inL + R)S_{22} = \phi(Q - in\phi),$$

and to solve the problem we must know S_{22} and Q for harmonic motions. These depend only upon the air column with the two diaphragms and may be found in two ways. To do this directly from the differential equations of the fluid motion, consider the tube of air and let S_0 and S_q be the stiffnesses of receiver and transmitter diaphragms alone, and also put:

ρ = mean density of fluid,
δP = increase of pressure over mean,
V = velocity potential in fluid,
$qV = \partial V/\partial x$,
f = impressed force on unit area of the receiver diaphragm.

The differential equations of the fluid motion are, for $p = in$

$$(n^2 + a^2q^2)V = 0; \quad \delta P = -in\rho V,$$

from which we get

$$V = e^{int}\left(A\cos\frac{nx}{a} + B\sin\frac{nx}{a}\right),$$

$$\delta P = -in\rho e^{int}\left(A\cos\frac{nx}{a} + B\sin\frac{nx}{a}\right)$$

The boundary conditions are:

At $x = 0$
$$S_0\xi_2 = f - \delta P,$$
$$p\xi_2 = qV.$$

At $x = l$
$$S_q\xi_3 = \delta P,$$
$$p\xi_3 = qV.$$

These four equations allow us to eliminate A and B and solve for ξ_2 and ξ_3 by means of:

$$\left(S_0 \cos\frac{nl}{a} - an\rho \sin\frac{nl}{a}\right)\xi_2 + S_q\xi_3 = f\cos\frac{nl}{a},$$

$$\left(S_0 \sin\frac{nl}{a} + an\rho \cos\frac{nl}{a}\right)\xi_2 - an\rho\,\xi_2 = f\sin\frac{nl}{a}.$$

From these we get:

$$S_{22} = \frac{(S_0S_q - a^2n^2\rho^2)\sin\frac{nl}{a} + an\rho(S_0 + S_q)\cos\frac{nl}{a}}{an\rho\cos\frac{nl}{a} + S_q\sin\frac{nl}{a}},$$

$$Q = \frac{hI \cdot an\rho}{an\rho\cos\frac{nl}{a} + A_q\sin\frac{nl}{a}},$$

and the problem is solved provided the resulting transcendental equations can be solved for the values of n and hI.

These values of S_{22} and Q are interesting in themselves: thus $S_{22} = 0$ gives the free vibrations of a pipe with arbitrary terminal conditions, and by putting, in the equivalent expression,

$$\tan\frac{nl}{a} = \frac{an\rho(S_0 + S_q)}{(an\rho)^2 - S_0S_q},$$

zero and infinite values of S_0, S_q, we get the frequencies of open and closed pipes. Other values give the effects of yielding ends.

There is one value of diaphragm stiffness which is unique and important Suppose $S_q = ian\rho$ so that the transmitter diaphragm offers only the resistance $a\rho = r_0$. Then

$$S_{22} = S_0 + inr_0,$$

$$\tan\frac{nl}{a} = i,$$

and we get the result that no finite free oscillations exist, so that no reflection takes place at S_q, all the energy sent out is absorbed, and the

tube behaves as one of infinite length. We therefore get the effect of an infinite column of fluid upon a vibrating diaphragm and the energy radiated to infinity. Hence r_0 may be called the radiation resistance of the fluid. For air it is about 40 C.G.S.

Although the equations of free vibration cannot be solved in general, the character of the solution can be seen. There will be a number of values of n which satisfy the frequency equation, and for each value of n a corresponding value of hI which is required to sustain the oscillations of that frequency.

These examples are sufficient to show the applications which may be made of this theory and method. Others, together with a treatment of non-linear connections, will be given in another paper.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

RADIATION AND ATOMIC STRUCTURE.[1]

BY R. A. MILLIKAN.

WHILE the study of the physical and chemical properties of matter has produced our present atomic theory and furnished most of the information which is available about the way in which the myriad molecular structures are built up out of their atomic constituents, it has been chiefly the facts of radiation which have provided reliable information about the inner structure of the atom itself. Indeed, during all the years in which the dogma of the indestructible and indivisible atom was upon the stage, it was the complexity of the spectra even of simple gases which kept the physicist in the path of truth, and caused him continually to insist that the atom could not be an ultimate thing, but rather that it must have a structure and a very intricate one at that—as intricate, in Rowland's phrase, as a grand piano.

Yet the evidence of spectroscopy, though tremendously suggestive in the series relationships brought to light between the frequencies of the different lines of a given substance, was after all most disappointing in that it remained wholly uninterpreted in terms of any mechanical model. No vibrating system was known which could produce frequencies related in the manner corresponding to the frequencies found even in the simplest of series, viz., the Balmer series of hydrogen. The discovery and study in the late nineties of corpuscular radiations of the alpha and beta type, with the changes in chemical properties accompanying them, merely served to confirm the century-old evidence of the spectroscope as to the fact of the complexity of the atom, and to educate the public into a readiness to accept it, without at first adding much information as to its nature. These studies did reveal, however, two types of bodies, the alpha and beta particles, as atomic constituents, though they said nothing at first as to their number, their arrangement, or their condition within the atom.

It was the study by Barkla of a radiation problem, namely the problem of the secondary X-radiations scattered by atoms, which furnished the first important evidence as to the number of electronic constituents within an atom. He found

[1] Presidential address delivered at the New York meeting of the Physical Society, December 27, 1916.

that the number of electrons which can act as scattering centers for X-rays is about half the atomic weight.[1] This conclusion was brilliantly confirmed by the simultaneous study in the Manchester laboratory of the scattering of the alpha rays in passing through matter,[2] and out of the converging evidence of these two types of research there emerged with considerable definiteness the Rutherford nucleus atom, consisting of a central, positively charged body of extraordinarily minute dimensions, its diameter being not over a ten thousandth of the diameter of the atom, surrounded, in the outer regions of the latter, by a number of negative electrons equal to about half the atomic weight. In this statement " the diameter of the nucleus " means the diameter of that portion of the atom which is found by experiment to be impenetrable to the alpha rays, while the diameter of the atom means the average distance of approach of the centers of two atoms in thermal encounters.

But it was again the study of a radiation problem which had to be called upon to furnish unquestionable information as to the exact value of this number, and at the same time to provide the most convincing evidence that we have of the general correctness of the conception of the nucleus atom.

In a research[3] which is destined to rank as one of the dozen most brilliant in conception, skillful in execution, and illuminating in results in the history of science, a young man but twenty-six years old threw open the windows through which we can now glimpse the sub-atomic world with a definiteness and certainty never even dreamed of before. Had the European war had no other result than the snuffing out of this young life, that alone would make it one of the most hideous and most irreparable crimes in history.

For the proof that there exist but 92 elements, from the lightest known one, hydrogen, to the heaviest known one, uranium, and that these are built up one from the other by the successive addition of one and the same electrical element to the nucleus, this proof comes alone from Moseley's discovery (checked and extended as it has been by de Broglie clear up to uranium) that the square roots of the characteristic X-ray frequencies of the elements progress by almost exactly equal steps from the lightest observable one to the heaviest. Moseley proved this in a general way for both the alpha and the beta emission lines of the hardest characteristic X-rays of the elements, the so-called K-rays, and also for the alpha and beta lines of the next softest series, the L series. Fig. 1 shows the now familiar regular progression of the wave-lengths of both the K and the L lines, as the elements which produce them rise in atomic weight and atomic number from top to bottom of the figure. These photographs, which are due to Siegbahn, are introduced merely to pave the way for the discussion and to enable comparison with Fig. 2, which represents the absorption spectra in various substances of the radiation emitted by tungsten. These beautiful photographs have just been sent me by de Broglie.[4] They are

[1] Barkla, Phil. Mag., 21, 648, May, 1911.

[2] Rutherford, Phil. Mag., 21, 669, May, 1911.

[3] Moseley, Phil. Mag., 26, 1024, Dec., 1913, and 27, 703, 1914.

[4] See Compt Rendu, 165, 87, 352, 1917.

taken by de Broglie's own method of the continuous rotation of the crystal of the X-ray spectrometer.

They show the general radiation of tungsten as a background in all the photographs, and the two K lines of tungsten (W) also in all, while the L series of tungsten appears in the upper one. The edge of the band marked $\frac{Ag}{K_A}$ is the exact point at which, with increasing frequency, the general radiation constituting the background begins to be absorbed by the silver atoms (atomic number 47) in the photographic plate, and the point for all frequencies above which it is absorbed in the remarkable manner discovered by Barkla to be characteristic of the absorption of X-rays. The edge marked $\frac{Br}{K_A}$ is the corresponding point for the bromine of the photographic plate whose atomic number is 35. These two points, characteristic of the AgBr emulsion of the plate, appear on most of the photographs. Absorption of course appears in the photographic plate as a lightening of the background, elsewhere as a darkening. The way in which this outer edge of the absorption band moves toward the central image as the atomic number increases in the steps Br 35, Mo 42, Ag 47, Cd 48, Sb 51, Ba 56, W 74, Hg 80, is very beautifully shown, in de Broglie's photographs, clear up to mercury, where the absorption edge is somewhat inside the shortest of the characteristic K radiations of tungsten. This latter line coincides, nearly if not exactly as will be shown in Table I., with the absorption edge of tungsten. There must be 12 more of these edges between mercury and uranium, and de Broglie has measured them clear up to thorium, thus extending the K series from N = 60 to N = 90, an enormous advance. The absorption edges become, however, very difficult to locate in the K region of frequencies because of their extreme closeness to the central image. But Fig. 3 shows the L-ray absorption bands in uranium and thorium. Fig. 4 shows how closely these absorption edges follow the Moseley law of equal steps for as many as twenty steps. In going from bromine, atomic number 35, to uranium, atomic number 92, the length of the Moseley step does change however by a few per cent. The data given in Table I. bring out the exceedingly interesting relation that the absorption edge coincides exceedingly closely in every case with the shortest emission K line of the absorbing substance, while in the L series one of the two absorption edges coincides exactly in every case with the shortest emission beta ray of the L series. The other coincides also in every case with an emission line, though the data is yet too meagre to permit of a generalization in the case of this second L absorption band.

Now it is these radiating and absorbing properties of atoms and these alone which justify a series of atomic numbers differing from and more fundamental than the series of atomic weights. Our present series of atomic numbers is simply this Moseley series of steps based on square root frequencies. It is true that a series of atomic numbers coinciding with the series of atomic weights was suggested earlier, indeed 100 years earlier, by Prout, and by many others since then, and it is true, too, that changes in the chemical properties of radio-

active substances accompanying the loss of alpha and beta particles led van den Broek,[1] just before Moseley's work appeared, to suggest that position in the periodic table might be a more fundamental property than atomic weight,[2]

TABLE I.

Comparison of K_A and K_B.

N.	Element.	K_A.	K_β.	N.	Element.	K_A.	K_β.
35	Br	.914	.914	53	I	.367	(.380)
37	Rb	.810	.813	55	Cs	.338	(.345)
38	Sr	.764	.767	56	Ba	.325	(.333)
40	Zr	.681	(.695)	57	La	.310	(.319)
41	Nb	.645	.657	58	Ce	.298	.(304)
42	Ma	.611	(.620)	78	Pt	.150	
46	Pd	.503	.503	79	Au	.147	
47	Ag	.479	.488	80	Hg	.143	
48	Cd	.458	(.466)	81	Tl	.139	
50	Sn	.419	(.419)	82	Pb	.135	
51	Sb	.399	.408	83	Bi	.130	
52	Te	.383	(.396)	90	Th	.098 about	

Comparison of L_A and L_B.

N.	Element.	L_A.	L_β.	N.	Element.	L_A.	L_β.
78	Pt	1.067	1.072	90	Th	.756	.750
79	Au	1.037	1.035	92	U	.719	.702
82	Pb	.945	.948				

but since this position is in some instances uncertain, and since the number of elements was wholly unknown, no definite numbers were or could be assigned to all the elements until Moseley's discovery was made, and the only evidence which we now have as to just how many elements there are between hydrogen and uranium, and as to just where each one belongs, is the evidence of the X-ray specta. It is true that between helium, atomic number 2, and sodium, atomic number 11, we have no evidence other than the order of atomic weights, the progression of chemical properties, and the number of known elements in this region, to guide us in completing the table, but since in the region of low atomic weights the progression in the Moseley table is always in agreement with the progression in the periodic table there can be little doubt of the correct number of each element even in this region which is as yet inaccessible to X-ray measurements. Moseley's name must then be set over against one of the most epoch making of the world's great discoveries. And I wish to call attention to some important conclusions as to atomic structure which are rendered extremely probable by it.

The first is this. If we may assume that the ordinary law of inverse squares holds for the forces exerted by the atomic nucleus on negative electrons near

[1] Van den Broek, Phys. Zeil., XIV., 32, 1913.

[2] This however was not a new suggestion, see, for example, A. J. Hopkins, J. Am. Ch. S., 1027, 1911.

it—and this time-honored law, so amply verified in celestial regions, has been fully verified for sub-atomic regions as well by the work done at the University of Manchester on the scattering of alpha rays—then the Moseley law that the square roots of the highest frequencies obtainable from different atoms are proportional to the nuclear charge[1] means, without any quantum theory, that the distances from the nucleus of each type of atom to the orbit of the inmost electron, if there be such an orbit, is inversely proportional to the charge on the nucleus, *i. e.*, to the atomic number. To see this it is only necessary to apply the Newtonian law connecting central force eE, orbital frequency n and radius a, namely

$$\frac{eE_1}{a^2} = (2\pi n)^2 ma, \quad \text{or} \quad \frac{n_1^2}{n_2^2} = \frac{E_1 a_2^3}{E_2 a_1^3} \tag{1}$$

and then to set as the statement of Moseley's experiment

$$\sqrt{\frac{n_1}{n_2}} = \frac{E_1}{E_2} \tag{2}$$

when there results at once from (1) and (2)

$$\frac{E_1}{E_2} = \frac{a_2}{a_1} \tag{3}$$

It may be objected that in the setting up of these relations I have made two assumptions, the one that the electrons rotate in circular orbits, and the other that the observed highest frequencies are proportional to the highest orbital frequencies. The first assumption is justified (*a*) by the fact that the recognized and tested principles of physics give us no other known way of providing a stable system, (*b*) by the experimental facts of light (Zeeman effect) and (*c*) by the phenomena of magnetism, especially the recent ones brought to light by Einstein and de Haas,[2] and by Barnett,[3] which well-nigh demonstrate the existence of permanent and therefore non-radiating electronic orbits. The exact circular form for the orbit is a secondary matter upon which, as will appear later, it is not necessary to insist. The second assumption, that the frequencies of the corresponding emission lines in the spectra of the various atoms are proportional to the orbital frequencies, is from a priori considerations probable and from certain theoretical considerations to be presented later necessary.

A second conclusion may be drawn from Moseley's discovery that the L lines progress in frequency from element to element just as do the K lines, the frequency being in each case between one seventh and one eighth as great. It is that, if there is a first or inmost electronic orbit, there must also be a second

[1] This is the proper statement of the Moseley law, as he himself *interpreted* his results. He knew and was careful to state that there is not an exact linear relation between the atomic number and the square roots of the frequencies, but the lack of exactness of (2) both as to straightness and to intercept may well be attributed to secondary causes (see below).

[2] Verh. d. D. Phys. Ges., XVII., p. 152, 1913.

[3] PHYS. REV., 6, 239, '15; also PHYS. REV., July, 1917.

one in all elements the radius of which is given by (1) to be about $(8)^{\frac{2}{5}}$ or four times as great as that of the first, provided orbital frequencies are in this case too assumed proportional to observed frequencies.[1]

Guided then by the newly discovered facts of X-radiations, and the unquestioned laws of force between electric charges, we get our first information as to the probable positions and conditions of some at least of the negative electrons within the atom.

Again, having found the highest natural frequency which can come from any element, viz., that from uranium, it is of extraordinary interest to inquire where, according to Moseley's law (2), the highest frequency line of the K series would fall for the lightest known element, hydrogen, whose nucleus should consist of but a single positive electron. This is obtained as shown in (2) by dividing the observed highest frequency of any element by the square of the atomic number. The shortest wave-length given out by tungsten, atomic number 74, is, according to de Broglie's measurements, $.177 \times 10^{-8}$ cm., and according to Hull's measurements, $.185 \times 10^{-8}$ cm. This gives for the shortest wave-length which could be produced by hydrogen, according to de Broglie $.177 \times 10^{-8} \times 74^2 = 97.9\mu\mu$, and according to Hull $101.3\mu\mu$. This is as close as could be expected, in view of the uncertainties in the measurements and the further fact that Moseley's steps are not quite exact, to the head of the ultra-violet series of hydrogen lines recently discovered by Lyman and located at $91.2\ \mu\mu$. There is every reason to believe, too, from the form of Balmer's series, of which this is the convergence wave-length, that this wave-length corresponds to the highest series frequency of which the hydrogen atom is capable. *It is fairly certain, then, that this Lyman ultra-violet series of hydrogen lines is nothing but the KX-ray series of hydrogen.* Similarly, it is equally certain that the LX-ray series of hydrogen is the ordinary Balmer series in the visible region, the head of which is at $365\ \mu\mu$. In other words hydrogen's ordinary radiations are its X-rays and nothing more. There is also an M series for hydrogen discovered by Paschen in the ultra-red, which in itself would make it probable that there are series for all the elements of longer wave-length than the L series, and that the complicated optical series observed with metallic arcs are parts of these longer wave-length series. As a matter of fact an M series has been found for six of the elements of high atomic number. Thus the Moseley experiments have gone a long way toward solving the mystery of spectral lines. They reveal to us clearly and certainly the whole series of elements from hydrogen to uranium, all producing spectra of remarkable similarity, at least so far as the K and L radiations are concerned, but scattered regularly through the whole frequency region, from the ultra-violet, where the K lines for hydrogen are found, clear up to frequencies $(92)^2$ or 8464 times as high. There can scarcely be a doubt that this whole field will soon be open to our exploration. How brilliantly, then, have these recent studies justified the predictions of the spectroscopists that the key to atomic structure lay in

[1] This assumption is in this csse inconsistent with the simple form of Bohr's theory, although that theory still gives the ratio of the radii of the first and second orbits 1 to 4.

the study of spectral lines. The prophets little dreamed, however, that the study of spectral lines meant the study of X-rays. But now, through this study, a sub-atomic world stands revealed to us in simpler form than could have been imagined. For the atoms are now seen to be, in their inner portions at least, remarkably similar structures, with central nuclei which are exact multiples of the positive electron, surrounded in each case by electronic orbits which have certainly, so far as the inner ones are concerned, practically the same relations in all the elements, the radii of all these orbits being inversely proportional to the central charge or atomic number.

So far nothing has been said about a quantum theory or a Bohr atom. The results have followed from the known properties of assumed circular electronic orbits combined with Moseley's experimental law, and supplemented by the single additional assumption that the observed frequencies of corresponding lines from different atoms are proportional to the orbital frequencies. If they suggest, however, that the experimental facts do not necessitate the quantum theory for their more complete interpretation, the consideration of the energy relations involved—these have been entirely ignored thus far—reveals at once the futility of that hope, or of that fear, according to the nature of your predilections with regard to theory of quanta. *For the experimental facts and the law of circular electronic orbits have limited the electrons to orbits of particular radii.* But the energy principle does not permit them to be so limited without a sudden or explosive loss of energy whenever the orbit is obliged to change. Suppose, for example, that a cathode ray strikes the atom and knocks out an electron from a particular orbit. When this or some other electron returns from infinity to this orbit, it must in this act adjust its energy to the only value which is consistent with this orbit and its characteristic frequency. Hence in the act of readjustment it must radiate a definite quantity of energy. Or again, suppose that the nucleus loses a beta ray through the radioactive process. Every electronic orbit must then adjust itself to the new value demanded by Moseley's law. But this it cannot do if its energy is conserved. The only way to permit it to do so is to let it radiate a definite amount of energy in the act of adjustment. This suggests that each emission of a beta ray by a radioactive substance must be accompanied by a whole series of characteristic gamma rays corresponding to each changed orbit. The emission of an alpha particle, on the other hand, would require an absorption rather than an emission of energy, since its egress diminishes rather than increases the nuclear charge. Perhaps this is why beta rays are always accompanied by gamma rays, while alpha rays are not so accompanied. This is, however, a speculation which does not immediately concern us here. The important conclusion, for the purposes of our present subject, is that Moseley's facts and unquestionable mechanics, combined with our two assumptions of circular orbits and radiation frequencies proportional in different atoms to corresponding orbital frequencies, lead inevitably to the explosive emission of energy in definite quantities accompanying orbital readjustments. And there is nothing particularly disturbing or radical about this conclusion either, for

we have no basis for knowing anything about how an electron inside an atom emits its radiation. The act of orbital readjustment would be expected to send out ether waves. The only difficulty lies in the conception of the stable, non-radiating orbits between which the change occurs, and whether or not we can see how such orbits exist, the experimental evidence that they do so exist is now very strong, and it is to further evidence for their existence, since that is the main point to be established if this theory of atomic structure is to prevail, that I now wish to direct your attention.

I have already mentioned the facts of magnetism and of the Zeeman effect which support the orbital point of view. But the strongest evidence is found in the extraordinary success of the Bohr atom, which was devised before any of these Moseley relationships, which have forced us to the essential elements of the Bohr theory,[1] had been brought to light. Bohr, however, was guided solely by the known character of the line spectra of hydrogen and helium, together with the rapidly growing conviction, now dissented from, so far as I know, by no prominent theoretical physicist, that the act of emitting electromagnetic radiation by an electronic constituent of an atom must, under some circumstances, though not necessarily under all, be an explosive process. To show what is the character of this evidence, let us consider first what are the essential elements in the Bohr theory and second what have been the accomplishments of that theory. Bohr's experimental starting point is the Balmer series in hydrogen the frequencies in which are exactly given by

$$\nu = N\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \tag{4}$$

n_1 having always, for the lines in the visible region, the value 2, and n_2 taking in succession the values 3, 4, 5, etc. As previously noted, Paschen had already brought to light a series in the infra red in which n_1 was 3 and n_2 took the successive values 4, 5, 6, etc. Lyman's discovery, subsequent to the birth of the Bohr atom, of an ultra-violet series of hydrogen lines in which n_1 is 1 and n_2 takes the values 2, 3, 4, etc., is not to be regarded as a success of the Bohr atom, but merely as a proof of the power of the series relationships to predict the location of new spectral lines. To obtain an atomic model which will predict these series relationships for the simplest possible case of one single electron revolving around a positive nucleus, Bohr assumed

A. A series of non-radiating orbits governed by equation (1). This is the assumption of circular orbits governed by the laws which are known to hold inside as well as outside the atom.

B. Radiation taking place only when an electron jumps from one to another of these orbits, the amount radiated and its frequency being determined by $h\nu = A_1 - A_2$, h being Planck's constant and A_1 and A_2 the energies in the two stationary states.

This assumption gives no physical picture of the way in which the radiation takes place. *It merely specifies the energy relations which must be satisfied.*

[1] N. Bohr., Phil. Mag., 26, 1, and 476, and 857, 1913. Also 29, 332, 1915; 30, 394, 1915.

The principle of conservation of energy obviously requires that the energy radiated be $A_1 - A_2$. Also this radiation must be assigned some frequency ν, and Bohr placed it proportional to the energy because of the Planck evidence that ether waves originating in an atom carry away from the atom an energy which is proportional to ν.

C. The various possible circular orbits for the case of a single electron rotating around a single positive nucleus to be determined by $T = \frac{1}{2}\tau hn$ in which τ is a whole number, n is the orbital frequency, and T is the kinetic energy of rotation. This condition was imposed by the experimentally determined relationship of the frequencies represented by the Balmer series.

It will be seen that, if circular electronic orbits exist at all, no one of these assumptions is in any way arbitrary. Each one of them is merely the statement of the existing *experimental* situation. The results derived from them must be correct if the original assumption of electronic orbits is sound. Now it is not at all surprising that A, B and C predict the sequence of frequencies found in the hydrogen series. They have been made on purpose to do it, *except for the numerical values of the constants involved.* It was this sequence which determined the form given to C. The evidence for the soundness of the conception of non-radiating orbits is to be looked for then, first *in the success of the constants, and second in the physical significance, if any, which attaches to assumption C.* If the constants come out right within the limits of experimental error, then the theory of non-radiating electronic orbits has been given the most critical imaginable of tests, especially if these constants are accurately determinable.

What are the facts? The constant of the Balmer series in hydrogen is known with the great precision attained in all wave-length determinations and has the value 3.290×10^{15}. From A, B and C it is given by the simplest algebra as

$$N = \frac{2\pi^2 e^2 E^2 m}{h^3} \tag{5}$$

I have recently redetermined e[1] with an estimated accuracy of one part in 1,000 and obtained again the value 4.774×10^{-10} which I published in 1913.[1] I have also determined "h" photoelectrically[2] with an error, in the case of sodium, of no more than .5 per cent., the value for sodium being 6.56×10^{-27}. The value found by Webster[1] by the method discovered by Duane and Hunt[2] is 6.53×10^{-27}. Taking the mean of these two results, viz.: $6{,}545 \times 10^{-27}$ as the most probable value, we get with the aid of Bucherer's value of e/m which is probably correct to one tenth per cent. $N = 3.294 \times 10^{15}$ *which agrees within a tenth per cent. with the observed value.* This agreement constitutes most extraordinary justification of the theory of non-radiating electronic orbits. It demonstrates that the behavior of the negative electron in the hydrogen atom is at least correctly described by the *equation* of a circular orbit. If this equa-

[1] R. A. Millikan, Proc. Nat'l Acad., April 1917.

[2] R. A. Millikan, PHYS. REV., VII., 362, 1916.

tion can be obtained from some other physical condition than that of an actual orbit it is obviously incumbent upon those who so hold to show what that condition is. Until this is done it is justifiable to suppose that the equation of an orbit means an actual orbit.

Again, the radii of the stable orbits for hydrogen are given easily from Bohr's assumptions as

$$a = \frac{\tau^2 h^2}{4\pi^2 m e^4}.$$

In other words, since n is a whole number, the radii of these orbits bear the ratios 1, 4, 9, 16, 25. If normal hydrogen is assumed to be that in which the electron is on the inmost orbit, $2a$ the diameter of the normal hydrogen atom, comes out 1.1×10^{-8}. The best determination for the diameter of the hydrogen molecule yields 2.2×10^{-8}, in extraordinarily close agreement with the prediction from Bohr's theory. Further, the fact that normal hydrogen does not absorb at all the Balmer series lines which it emits is beautifully explained by the foregoing theory, since according to it normal hydrogen has no electrons in the orbits corresponding to the lines of the Balmer series. Again, the fact that hydrogen emits its characteristic radiations only when it is ionized favors the theory that the process of emission is a process of settling down to a normal condition through a series of possible intermediate states, and is therefore in line with the view that a change in orbit is necessary to the act of radiation. Similarly, the fact that in the stars there are 33 lines in the Balmer series, while in the laboratory we never get more than 12 is easily explicable from the Bohr theory, but no other theory has offered even a suggestion of an explanation. But while these qualitative successes of the Bohr atom are significant it is the foregoing numerical agreements which constitute the most compelling of evidence in favor of the single arbitrary assumption contained in Bohr's theory, viz.: the assumption of non-radiating electronic orbits.

Another triumph of the theory is that the assumption C, devised to fit a purely empirical situation, viz., the observed relations between the frequencies of the Balmer series is found to have a very simple and illuminating physical meaning, viz., the atomicity of angular momentum. Such relationships do not in general drop out of empirical formulae. When they do we usually see in them real interpretations of the formulae—not merely coincidences.

Again the success of a theory is often tested as much by its adaptability to the explanation of deviations from the behavior predicted by its most elementary form as by the exactness of the fit between calculated and observed results. The theory of electronic orbits has had remarkable successes of this sort. Thus it predicts, as can be seen from 4, 5 and 3, the relationship which we assumed, viz., that for corresponding lines (like values of n_1 and n_2 in 4) the orbital frequencies n are proportional to the observed frequencies ν, and similarly it predicts the Moseley law (2). But this latter relation, which is the only one of the two which can be directly tested, was found inexact, and it should be inexact when there is more than one electron is the atom, as is the case save

for hydrogen atoms and for such helium atoms as have lost one negative charge, and that because of the way in which the electrons influence one another's fields. It will probably be found to break down completely for very light atoms like those of lithium. The more powerful the nucleus, however, and the closer to it the inner orbit the smaller should this effect be. Now precisely this result is observed. The Moseley law holds most accurately when tested for hydrogen and the elements of highest atomic number and much less accurately when tested for hydrogen and aluminum or magnesium. Similarly the ratio between the frequencies of the α and β lines of the K series approaches closer to the theoretical value (that for hydrogen) the higher the atomic number of the element.

Again, it is now well known that the α, β, and γ lines in the characteristic X-ray spectra are not single lines as required by the simple theory. Accordingly Sommerfeld[1] extended Bohr equations in the endeavor to account for this structure on the basis of ellipticity in some of the orbits, and Paschen[2] by measurements on the structure of the complex helium lines has obtained so extraordinary checks upon this theory that e/m comes out from his measurements to within a tenth per cent. of the accepted value.

A further prediction made by the theory and discovered as soon as looked for was the relation between the lines of two succeeding series of this sort.

$$\nu_{K\beta} - \nu_{K\alpha} = \nu_{L\alpha}$$

This should hold accurately from the energy relations between the orbits whether there be one or many electrons in the atoms. I have been able to find no case of its failure, though the data upon which it may be tested is now considerable. I have also recently pointed out[3] that it is equivalent to the well-known Rydberg-Schuster law[4] which has been found to hold quite generally among optical series. Finally the ionizing potential of hydrogen is given by Bohr's equations as 13.54 volts while experiment yields 11.5 volts. This discrepancy is no way prejudices the theory, but rather lends it support, for the computed value is for the hydrogen atom while the observed value relates to the hydrogen *molecule* which, in view of the repulsions between its two negative electrons might be expected to be ionized more easily. Similarly the computed value for helium which has lost one negative electron is 52.4 volts, but the neutral helium atom is found experimentally to be ionized at the much lower value 20.5 volts. That Bohr computed this latter value at 27 instead of 20.5 volts is not at all serious, since he had to make very particular assumptions to obtain this result.

If then the test of truth in a physical theory is large success both in the prediction of new relationships and in correctly and exactly accounting for old ones, the theory of non-radiating orbits is one of the well-established truths of

[1] Annalen der Physik, 51, 1, 1916.

[2] Annalen der Physik, Oct., 1916.

[3] PHYS. REV., May, 1917, presented before Amer. Phys. Soc., Dec. 1, 1916.

[4] Baly's Spectroscopy, p. 488.

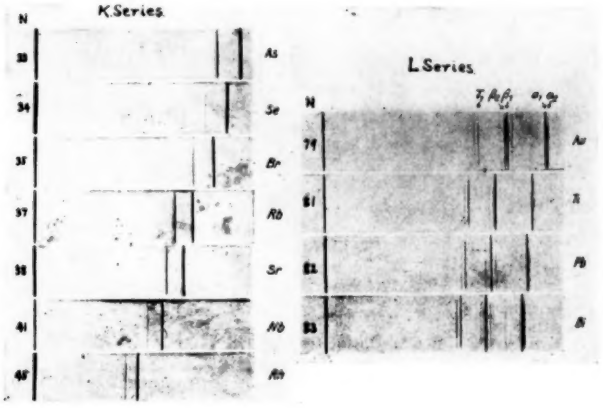

Fig 1.

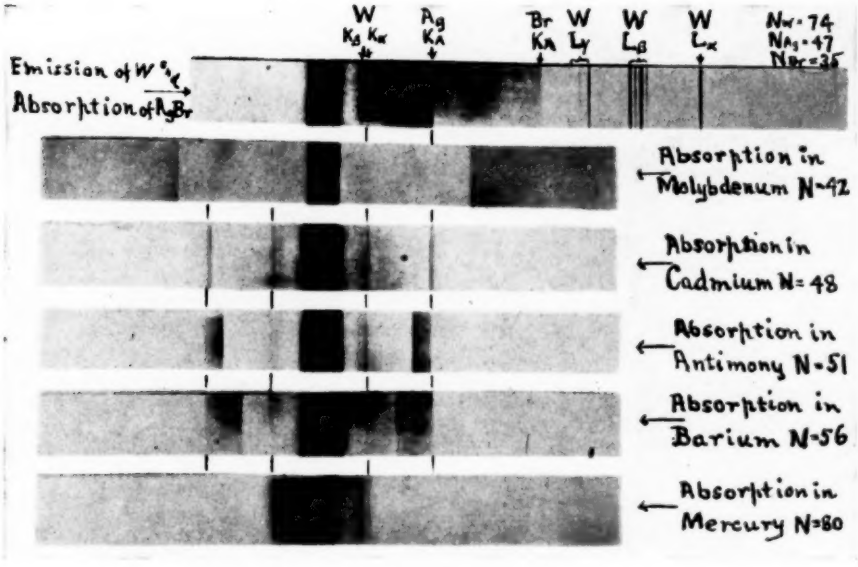

Fig. 2. Showing absorption (in K region) of general radiation of tungsten by various substances.

R. A. MILLIKAN.

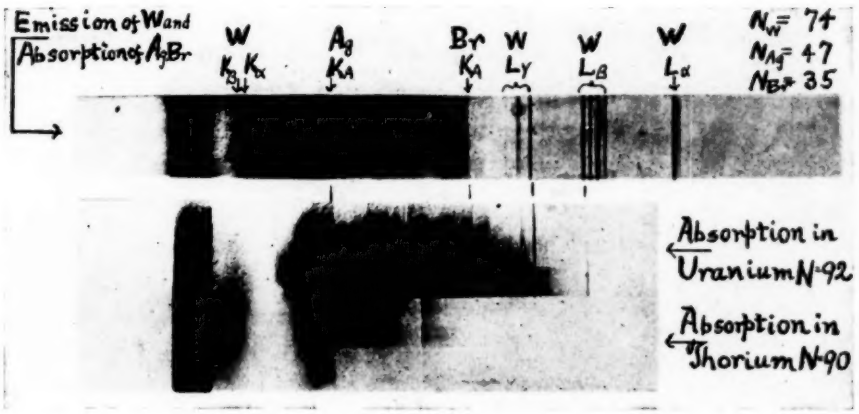

Fig. 3. Showing absorption (L region) by uranium and thorium.

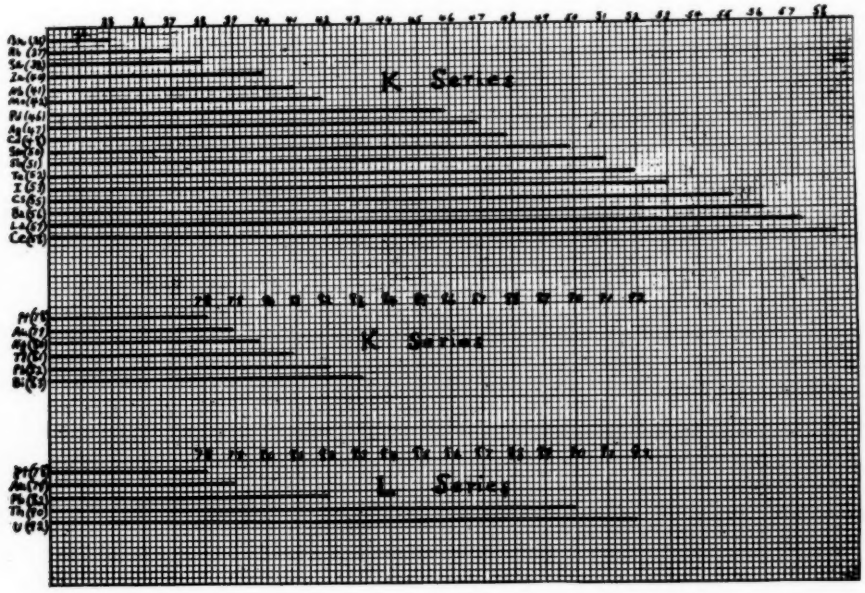

Fig. 4.

R. A. MILLIKAN.

modern physics. For the present at least it is truth, and no other theory of atomic structure need be considered until it has shown itself able to approach it in fertility. I know of no competitor which is as yet even in sight. I am well aware that the facts of organic chemistry seem to demand that the valence electrons be grouped in certain definite equilibrium positions about the periphery of the atom, and that at first sight this demand appears difficult to reconcile with the theory of electronic orbits. As yet, however, there is no necessary clash. Hydrogen and helium present no difficulties, since the former has but one valency, and the latter none. It is to these atoms alone that the unmodified Bohr theory applies, for it treats only the case of a single negative electron rotating about a positive nucleus. That the K radiations of the heavy elements are so accurately predictable from those of hydrogen indicates indeed that close to the nucleus of these elements there lie electrons to which the Bohr theory fairly accurately applies, but the radiations give us no information about the conditions or behaviors of the external electrons which have to do with the phenomena of valency, and we have investigated but little the radiating properties of the atoms which possess but few electrons. A further study of the behavior with respect to X-rays of the elements from lithium, atomic member 3, to magnesium, atomic number 11, may be expected to throw new light on this problem.

It has been objected too that the Bohr theory is not a radiation theory because it gives us no picture of the mechanism of the production of the frequency ν. This is true, and therein lies its strength, just as the strength of the 1st and 2nd laws of thermodynamics lies in the fact that they are true irrespective of a mechanism. The Bohr theory is a theory of atomic structure; it is not a theory of radiation, for it merely states what energy relations must exist when radiation, whatever its mechanism, takes place. As a theory of atomic structure, however, it is thus far a tremendous success. The radiation problem is still the most illusive and the most fascinating problem of modern physics. I hope to discuss it at a later time.

AMPLIFICATION OF THE PHOTOELECTRIC CURRENT BY THE AUDION.[1]

BY JAKOB KUNZ.

THE photoelectric cell is used already as a photometer for many scientific investigations, for instance in stellar photometry, in plant physiology, in researches on phosphorescence, on transmission, absorption, reflexion and radiation of light in various forms. It would find further applications, even for technical purposes, if the photoelectric current were larger. The writer has some time ago constructed a photoelectric relay, where the primary photoelectric current was increased considerably by a second electric field in the cell. However this relay has not been studied and developed sufficiently and it was

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 20–21, 1917.

found that the audion, which has already so many important applications, amplifies the photoelectric current to a higher degree than the relay. The arrangement of the apparatus is given in the following figure, where P represents the photoelectric cell, G_1 and G_2 two galvanometers, B_1, B_2, B_3 batteries of 120, 20 and 8 volts; A the audion. The photoelectric cell was illuminated

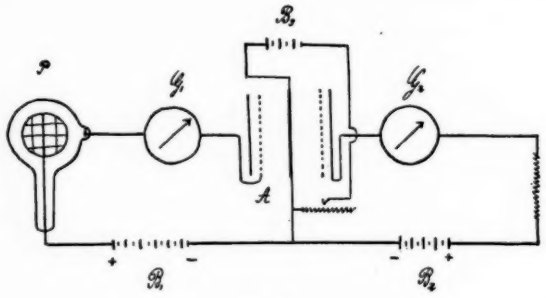

Fig. 1.

by an incandescent lamp of 2 candles at various distances from 30 to 170 cm. from the cell; the battery B_3 supplies the heating current of the filament of the audion. The galvanometer G_1 of the primary circuit was 32 times more sensitive than G_2 of the secondary circuit. The amplification of the photoelectric current by the audion depends largely on the temperature of the incandescent filament; the higher the temperature, the greater the secondary current, as will be seen from the following readings.

34, 5	102
34, 0	130
34	180
33	250
33	500

When the deflection of the secondary galvanometer was 500, the temperature of the filament was that of beginning white heat; the secondary deflection is 15 times larger than the primary, or the secondary current is 480 times larger than the primary photoelectric current. And it was easy by raising the temperature to amplify the photoelectric current 1000 times. With higher temperatures the secondary currents become less steady. A small variation of illumination produces a large variation in the secondary deflection. The voltage applied to the photoelectric cell connected with the audion can be raised above the point, where the glow in the cell sets in when independent of the audion.

LABORATORY OF PHYSICS,
UNIVERSITY OF ILLINOIS,
URBANA, ILLINOIS, April, 1917.

High Vacuum Spectra from the Impact of Cathode Rays.[1]

By Louis Thompson.

E. P. LEWIS, A. S. King and others have described experiments on the production of metallic spectra by cathodo-luminescence.

R. H. Goddard has devised a means[2] of increasing the light in one section of the tube, due to the impact of cathode rays, thus making it possible to work with much higher vacua. The method consists essentially in the use of a magnetic field applied parallel to the axis of two small negatively charged plates, which also serve as cathodes. The combined effect of the electric and magnetic fields is to cause the electrons to assume a closed helical path in the very limited region between these plates. This results in a small but bright cylinder of light (between *A*, *B* in the figure) even at extremely low pressures, where without the field, the illumination would be so faint that satisfactory exposures would be impossible.

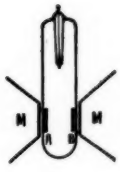

Fig. 1.

In addition to the advantage of having sufficient light for comparatively short exposures at high vacua, there are no temperature effects and the pressures are definitely known, especially when working with substances which are normally gaseous. The use of capillary tubes for high vacuum work, while possible, gives spectra which depend largely upon temperature and current density.

At high vacua and with temperature effects absent, simple spectra are likely to result. A recent paper by Mallik and Das[3] emphasizes this point.

A number of substances are being examined. The first exposures were made with mercury vapor and tellurium, the mercury at pressures down to that corresponding to a three-inch parallel spark.

Compared with the ordinary vacuum tube discharge the spectrum is simple and the relative intensities are noticeably different. The important series lines are prominent in the visible region. In the ultra-violet only 3131, 3125 and 2536 are strong. 2536 is the brightest line in the spectrum and seems to become relatively stronger as the vacuum increases.

Experiments are being made with hydrogen in an attempt to determine whether at high vacua and with the increased illumination, the extended Balmer series, which has only appeared in certain stellar spectra, can be found in a discharge tube.

The magnetic field used in the work is not strong enough to produce a detectable effect on the spectrum.

Clark University,
Worcester, Mass.

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 20–21, 1917.

[2] Described in U. S. Patent 1,137,964.

[3] Phil. Mag., March, 1917.

A PROPOSED METHOD FOR THE PHOTOMETRY OF LIGHTS OF DIFFERENT COLORS. —III.[1]

BY IRWIN G. PRIEST.

TWO papers under the above title[2] have already been communicated to the Physical Society by the author. The purposes of the present paper are:

1. To present some data on spectral distribution in order to further elucidate and substantiate the method.

2. To publish, for reference, a table of numerical values of the method factor mentioned in the first paper and explicitly defined in the second paper as

$$R = \frac{\int_{400}^{740} VE \sin^2(\phi - \alpha) d\lambda}{\int_{400}^{740} VE d\lambda}.$$

3. To note some advantages and possible applications of the method.

1. *The Relative Spectral Distribution of Lights Color-matched by the Proposed Method.*—The essential feature of the method is that light from a comparison source of known spectral distribution is modified by passage through a quartz plate between nicol prisms so as to match the color of the source being tested. The quartz plate and the nicols constitute, in effect, a " color screen " of readily adjustable spectral transmission, the relative transmission for any wave-length being given by[3]

$$\sin^2(\phi - \alpha).$$

Typical curves showing values of this expression as a continuous function of λ for various values of ϕ (" spectral transmission curves ") are shown in Fig. 1.

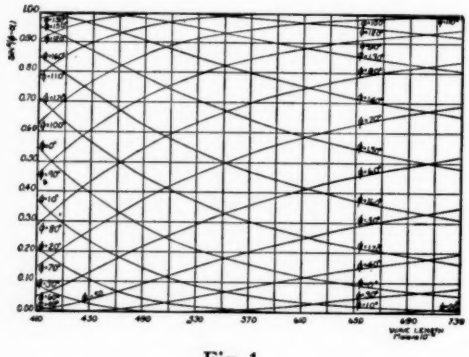

Fig. 1.

Relative transmission of a system composed of a 1 mm. plate of quartz between nicol prisms. α = rotation of plane of polarization by the quartz plate (a function of wave-length); ϕ = rotation of analyzing nicol from position for extinction (quartz removed). (Both α and ϕ are measured clockwise from observer's position).

[1] Abstract of a paper presented (by title) at the Washington meeting of the Physical Society, April, 1917.

[2] Am. Phys. Soc., Wash., April, 1915; PHYS. REV. (2), 6, 64. Am. Phys. Soc., N. Y., Dec., 1916; PHYS. REV. (2), 9, 341 (for erratum see p. 580).

[3] For definition of symbols see PHYS. REV., 9, 343.

In the previous papers it was merely stated that a sensibly perfect color-match had been obtained. Fig. 2 in the present paper compares the spectral

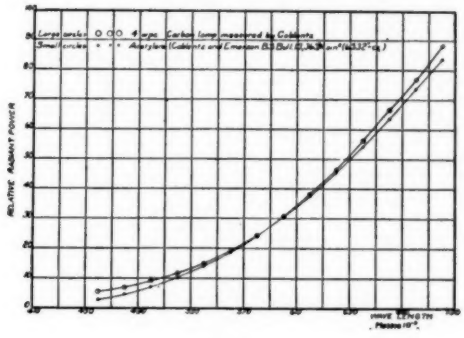

Fig. 2.

Two spectral radiation distributions giving an empirical color match in the relative candlepower determinations reported in paper No. II. of this series.

distribution in light from the carbon lamp at 4 w.p.m.h.c.[1] with the spectral distribution of the light indirectly made to color-match it by the proposed method in the determination of relative candlepowers reported in the second paper cited above.

Fig. 3 shows the theoretical possibility of color-matching, by this method,

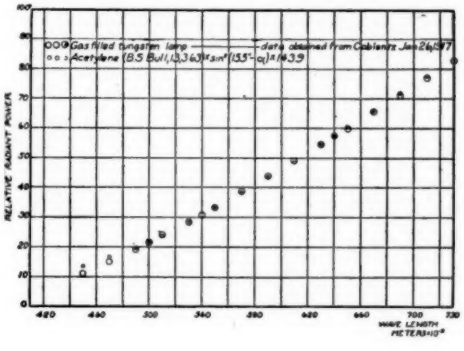

Fig. 3.

Illustration of the matching of a given spectral radiation distribution by a distribution computed by the rotatory dispersion method.

the light from a gas-filled tungsten lamp. This does not represent an empirically determined color-match, but merely compares the spectral distribution of the gas filled lamp,[2] with that of acetylene as modified by the quartz-nicol system, the thickness of quartz and the angle ϕ having been theoretically chosen to give the desired spectral transmission. The exact efficiency of the gas-filled lamp in this case is not known, but was probably about 15 lumens per watt.

[1] Determined radiometrically by W. W. Coblentz and communicated to the author.

[2] Radiometrically determined by W. W. Coblentz.

Fig. 4 compares the radiometrically determined spectral distribution[1] of a gas-filled lamp at 15.6 lumens per watt[2] with the spectral distribution of the light empirically found to color-match it by this method, the match being made by the author using the Arons Chromoscope.[3]

The dotted and dashed curves in Fig. 5 show the spectral distributions of

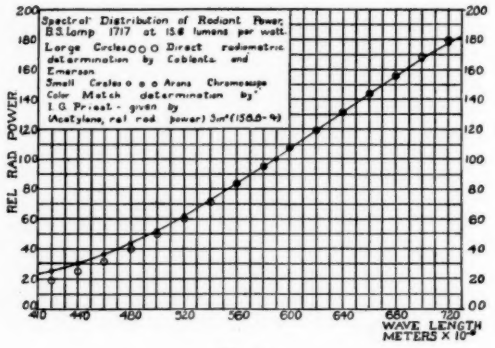
Spectral Distribution of Radiant Power, B.S. Lamp 1717 at 15.6 lumens per watt.
Large Circles o o o Direct radiometric determination by Coblentz and Emerson.
Small Circles o o o Arons Chromoscope Color Match determination by I. G. Priest - given by (Acetylene, rel red power) S=f(158.0-9)
REL. RAD. POWER
WAVE LENGTH METERS X 10⁻⁹
400 440 480 520 560 600 640 680 720

Fig. 4.

lights found, by this method, to color-match a gas-filled lamp at 22.3 lumens per watt and at 22.0 lumens per watt.[4]

The solid curve from Luckiesh, " Color," page 21, is given for comparison.

When it is considered that the efficiency of a gas-filled lamp can not be taken as a reliable specification of its color, and that the photometry of these lamps is a matter of considerable uncertainty, this discrepancy appears hardly greater

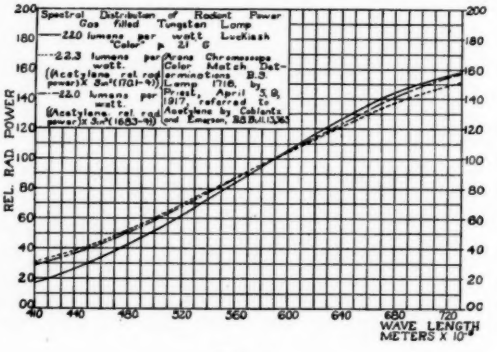
Spectral Distribution of Radiant Power
Gas filled Tungsten Lamp
22.0 lumens per watt. Luckiesh "Color" p. 21 G
22.3 lumens per watt. (Acetylene rel red power) S=f(170.1-9)
22.0 lumens per watt. (Acetylene rel red power) S=f(168.3-9)
Arons Chromoscope Color Match Determinations B.S. Lamp 1716, by I. G. Priest, April 3, 1917, referred to Acetylene by Coblentz and Emerson, B.S.B.U.I.385
REL. RAD. POWER
WAVE LENGTH METERS X 10⁻⁹
400 440 480 520 560 600 640 680 720

Fig. 5.

than might be expected. It will be noted that the agreement of curves in Fig. 4, where the data are strictly comparable (pertaining to the *same lamp*), is considerably better.

It will be understood, of course, that the author has no idea of here testing

[1] By Coblentz and Emerson, Bureau of Standards.

[2] By Crittenden and Taylor, Bureau of Standards.

[3] Ann. der Phys. 39, 545, 1912.

[4] By Crittenden and Taylor, Bureau of Standards.

the accuracy of spectral distributions determined radiometrically or spectrophotometrically. The purpose of presenting this data is merely to show how closely this method of empiric *color-matching* does, in fact, give a spectral match. Those familiar with the subject will readily see that this method of color-matching gives better spectral matches than are obtained by colored glasses, which have been used for the same purpose.

A given source may be color-matched using quartz plates of different thicknesses, each plate, of course, requiring a different value of ϕ to give the color-match. For example, with acetylene as a comparison source, a gas-filled tungsten lamp at 12.3 lumens per watt may be color-matched with the following thicknesses of quartz and corresponding values of ϕ:

Thickness, mm.	ϕ, degrees.
0.50	162.4
.75	157.9
1.00	154.6

The spectral distribution curves from these three sets of data are much the same; but have, indeed, slightly different curvatures, so that one of them may match the true spectral distribution of the lamp better than the others. Further consideration is being given to the choice of the quartz thickness best suited to give a very close spectral match where that is desired, but 1.000 mm. appears very satisfactory for the photometry of the incandescent lamps now in use (carbon, vacuum tungsten and gas-filled tungsten).

2. *Table of the Method Factor.*—In the previous papers, it was pointed out that computations in terms of this method, while apparently quite involved, could be made very simple by the use of permanent reference tables of the " method factor," R. The labor of preparing such a table, based on the most recent and reliable data for " visibility " and " spectral distribution of radiant power " has now been completed,[1] and the table is presented herewith in the hope it will be useful to any who care to investigate or use the method.

For illustrative purposes, the form of the function R is shown in Fig. 6.

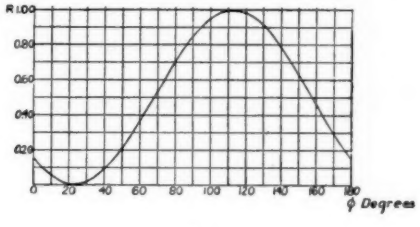

Fig. 6.

All steps in the preparation of this table have been carefully checked and the author trusts that it will be found reliable. He hopes however that some one may find interest enough in the subject to check this table entirely independently assuming nothing except the same fundamental data for E, V and α, and the arbitrary values for ϕ.

[1] Graphic integration and computation by H. J. McNicholas, J. T. Filgate and H. E. Cole.

As the subject develops, it may be later found desirable to know R for some particular values of ϕ more accurately than it is given in the present table. The author hopes to undertake such determinations later. Before this method can be generally adopted, it will of course be necessary for those interested and in authority to agree upon standard values for V and E as used in the formula for R. Instead of taking E for acetylene, it may be best to refer directly to a black body at some specified temperature.

3. *Notes on Advantages and Applications of the Method.*—(*a*) It is evident from the data presented above that this method is superior to the color glass method from the point of view of obtaining a close spectral match as well as a "color-match."

(*b*) Selective transmission obtained and controlled in this way is universally reproducible and subject to fine adjustment, while that obtained by glasses, is, in general, neither.

(*c*) Spectral transmission determined by this method is more reliable than that of a glass determined by means of the spectrophotometer; and, by use of permanent tables, may be more readily obtained.

(*d*) The data obtained in determining candlepower may be readily translated into a significant specification of the color of the light being tested.

(*e*) The method is applicable to the production of "artificial daylight" from tungsten lamps, giving a much better spectral match than has been obtained by the use of blue glass. The author is preparing a separate paper on this subject.

(*f*) At the request of Dr. N. E. Dorsey, application of this method to determine the brightness of very faint greenish fluorescent screens is being attempted. A satisfactory color-match has been found.

(*g*) It is obvious that the photometer described in the preceding paper in this series, may be used as a pyrometer, and might be calibrated to read temperatures directly, but the author ventures no opinion as to its value for this purpose.

NATIONAL BUREAU OF STANDARDS,
April 17, 1917.

THE METHOD FACTOR R AS A FUNCTION OF ϕ

Computed by H. J. McNicholas, J. T. Filgate and H. E. Cole, Dec., 1916–Jan., 1917.

$$R = \frac{\int_{400}^{740} VE \sin^2(\phi - \alpha) d\lambda}{\int_{400}^{740} VE \, d\lambda}$$

assuming the following functions of λ:

V = Relative Visibility, Coblentz and Emerson, Phys. Rev. 9, 88.

E = Relative Radiant Power Acetylene Flame, Coblentz & Emerson, B. S. Bull 13, 363.

α = Specific Rotation of Quartz (Degrees/mm), Landolt, Op. Dreh. 2nd Ed., p. 128; and Landolt Börnstein Tables, 1913 Ed., p. 1062.

(This table was constructed by graphic interpolation from values determined by graphic integration at intervals of 5°. The values tabulated are means of two independent interpolations. They are considered reliable to about 0.001.

ϕ.	R.	ϕ.	R.	ϕ.	R.	ϕ.	R.
1°	0.1425	46°	0.1545	91°	0.856	136°	0.844
2	132	47	1675	92	867	137	831
3	121	48	1805	93	879	138	818
4	1105	49	194	94	889	139	805
5	1005	50	209	95	899	140	791
6	091	51	222	96	9095	141	777
7	081	52	2365	97	9195	142	7615
8	072	53	251	98	9285	143	747
9	064	54	266	99	938	144	7315
10	056	55	2815	100	946	145	716
11	048	56	297	101	954	146	700
12	041	57	3135	102	9605	147	6845
13	034	58	330	103	9675	148	668
14	028	59	347	104	973	149	652
15	023	60	364	105	978	150	636
16	018	61	3805	106	983	151	620
17	014	62	397	107	9865	152	6035
18	011	63	4135	108	990	153	586
19	008	64	4305	109	993	154	570
20	006	65	447	110	995	155	552
21	004	66	4645	111	9955	156	5355
22	004	67	482	112	9955	157	518
23	0035	68	4995	113	995	158	5005
24	004	69	5165	114	994	159	4825
25	005	70	534	115	9925	160	4645
26	006	71	551	116	991	161	448
27	008	72	5675	117	9885	162	430
28	0115	73	585	118	9865	163	413
29	0145	74	6015	119	984	164	3955
30	5185	75	6185	120	980	165	378
31	0235	76	6355	121	9765	166	361
32	029	77	652	122	9715	167	345
33	0355	78	6685	123	9665	168	329
34	042	79	685	124	960	169	3125
35	049	80	7015	125	953	170	2965
36	056	81	717	126	9465	171	2805
37	064	82	733	127	9385	172	266
38	072	83	7485	128	9305	173	2505
39	081	84	763	129	922	174	236
40	090	85	7775	130	9125	175	222
41	099	86	7915	131	902	176	2075
42	109	87	8055	132	891	177	1935
43	1195	88	819	133	8805	178	1805
44	1305	89	8325	134	8685	179	167
45	142	90	8445	135	856	180	1545

NEW BOOKS.

A System of Physical Chemistry. By WILLIAM C. McC. LEWIS. New York: Longmans Green and Company, 1916. In two volumes. Vol. I., pp. xiv +523; Vol. II., pp. vii+552.

As this book belongs to the well-known series of text-books on physical chemistry which includes Findlay's " Phase Rule," Mellor's " Chemical Statics and Dynamics," and Young's " Stoichiometry," one naturally expects a high standard of excellence. Although opinions may differ as to whether the present work deserves as high a rating as the others just mentioned, there can be no doubt that the author has performed a difficult task with remarkable success. In respect to completeness and extent of ground covered, especially in the more recent developments of the subject, this book is not equalled, so far as known to the reviewer, by any other text-book of physical chemistry originally written in English.

Some previous knowledge of the subject is assumed and a few of the topics emphasized in the average text are omitted, or at least not separately discussed. We look in vain for sections on thermochemistry, the periodic system, determination of atomic weights, relations between physical properties and chemical constitution, and several other familiar titles. On the other hand the author has aimed to include " some account of recent investigation " and cites in the preface, as examples, the sections dealing with the structure of the atom, the theory of concentrated solutions, capillary chemistry, Nernst's theorem of heat, the thermodynamics of photochemical reactions, and the application of the Planck-Einstein " Energie Quanta " to the specific heat of solids. How thoroughly these subjects are treated can be inferred from the fact that about 125 pages of text are devoted to the last three alone. In general, the author has been very conscientious in including and giving ample space to the newer developments of the subject, but there are some exceptions. For example, in dealing with the structure of the atom the theories of J. J. Thomson and of Nicholson are each treated at length, while the much more important theory of Rutherford is barely mentioned in a foot-note. It is also surprising, and very much to be regretted, that in so large a book a few pages have not been devoted to the recent classification of the radio-elements according to chemical properties and atomic numbers, and to the conception of isotopes, subjects of great importance and exceptional interest.

The arrangement of the subject matter is novel. Volume I. is entitled " Kinetic Theory " and Volume II., " Thermodynamics and Statistical Mechanics." Underlying this arrangement, which we are told is merely arbitrary and intended to make the book more readable, is the author's system of classification which is presented in tabular form at the beginning of the book. The

actual arrangement of the material seems to be a sort of compromise between these two divergent plans of classification and as a result many topics treated in the first volume have to be taken up again in the second. This system is confusing to the uninitiated, and its advantages, to say the least, are not apparent.

In general, the author presents his subject matter with commendable clearness, but perhaps overemphasizes his lack of personal bias, and the statements of more or less conflicting views are not always accompanied by any actual sifting of the evidence. This, and the peculiarities of arrangement, seem to the reviewer the most evident faults in an otherwise excellent and useful book.

R. G. V. N.

Electrical Engineering, Advanced Course. By ERNST JULIUS BERG. New York: McGraw-Hill Book Company, Inc., 1916. Pp. viii+332.

The author has made a constructive contribution in the field between the more usual treatment of alternating currents, as given by Steinmetz, Bedell and Crehore and others, and advanced electrical theory as given by Maxwell, Heaviside, Webster and others. Although he has not given us a complete bridge between the two, he has supplied some helpful stepping stones and has performed a useful service.

F. B.

Color and its Applications. By M. LUCKIESH. New York: D. Van Nostrand Co., 1915. Pp. xii+357. Price, $3.00.

In the words of the author: ". . . the desire has been frequently expressed for a book that treated the science of color as far as possible from the viewpoint of those interested in the many applications of color." The object of the present volume is to meet this demand.

The opening chapters are devoted to a discussion of fundamental concepts concerning the nature of light and color. This is followed by a treatment of color analysis and synthesis and allied subjects The final chapters deal with the practical applications of the preceding theoretical considerations. Such subjects as Color in Lighting, Color Effects for the Stage and Displays, Color Phenomena in Painting, Color Matching, Art of Mobile Colors and Colored Media are discussed.

Considering the book as a whole, it serves well the purpose for which it was written. Since its appeal is to the general public, the author has avoided wisely the use of mathematics. While a number of misstatements occur in the earlier chapters, the treatment is, as a rule, clear. Numerous cuts and half-tones illustrate the text admirably. The later chapters, which deal with practical applications and which embody much of the author's own work, form by far the most important part of the book.

By the choice of large type and unglazed paper, the author has given a unique application of some of the principles laid down in the text.

A. H. P.

Concise Technical Physics. By J. LORING ARNOLD. New York: McGraw-Hill Book Company, Inc., 1916. Pp. viii+275. Price, $2.00.

To quote from its preface: "This book is an embodiment of actual classroom work in the first college course in theoretical physics. It is intended primarily for use in schools of engineering, but may be used in other collegiate institutions equally well." The title raises false hopes, for the interesting but very difficult problems of technical physics are not the subject treated. The book should be called "Physics for Engineering Students." Numerous instances of the author's lack of a thorough command of his subject prevent the reviewer, much to his regret, from recommending this book.

E. B.

Principles of Alternating Current Machinery. By RALPH R. LAWRENCE. New York: McGraw-Hill Book Company, 1916. Pp. xvii+614.

This book is not a description of alternating current machinery, nor is it a treatise on the theory of alternating current; its subject matter is exactly as indicated in the title—the principles of alternating current machinery. The author discusses synchronous generators, static transformers (the adjective, but not the treatment, is quite out of date), synchronous motors, parallel operation of alternators, synchronous converters, polyphase induction motors, single phase induction motors, series and repulsion motors. The discussion is clear and is given with great thoroughness—almost exhaustive thoroughness so far as principles go. The book will prove useful both to student and engineer.

F. B.

Preliminary Mathematics. By F. E. AUSTIN. Hanover, N. H., 1917. Pp. i+169. Price $1.20. (*Received.*)

Analytic Geometry. By W. A. WILSON and J. I. TRACEY. New York: D. C. Heath and Co., 1915. Pp. x+212. (*Received.*)

A Chemical Sign of Life. By SHIRO TASHIRO. Chicago: The University of Chicago Press, 1917. Pp. ix+142. Price, $1.00. (*Received.*)

The Biology of Twins (Mammals). By HORATIO HACKETT NEWMAN. Chicago: The University of Chicago Press, 1917. Pp. ix+189. Price, $1.25. (*Received.*)

Finite Collineation Groups. By H. F. BLICHFELDT. Chicago: The University of Chicago Press, 1917. Pp. xi+193. Price, $1.50 net. (*Received.*)

Leçons sur Les Fonctions Elliptiques en vue de Leurs Applications. By R. DE MONTESSUE DE BALLORE. Paris: Gauthier-Villars et Cie, 1917. Pp. x+267. Price, 12 fr. (*Received.*)

A Laboratory Course of Practical Electricity for Vocational Schools and Shop Classes. By MAURICE J. ARCHBOLD. New York: The Macmillan Company, 1916. (*Received.*)